

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-303937

(43)Date of publication of application : 31.10.2001

(51)Int.Cl.

F01N 3/20
 B01D 53/94
 F01N 3/08
 F02D 41/04
 F02D 41/12
 F02D 45/00

(21)Application number : 2000-275725

(71)Applicant : TOYOTA MOTOR CORP

(22)Date of filing : 11.09.2000

(72)Inventor : ASANUMA TAKAMITSU
 TANAKA TOSHIAKI

(30)Priority

Priority number : 2000040837

Priority date : 18.02.2000

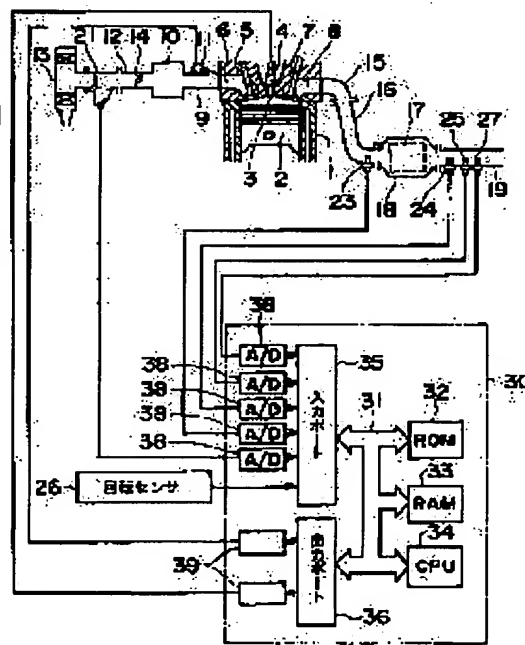
Priority country : JP

(54) EXHAUST EMISSION CONTROL DEVICE FOR INTERNAL COMBUSTION ENGINE

(57)Abstract:

PROBLEM TO BE SOLVED: To detect the degree of thermal deterioration of a storage and reduction type NOx catalyst.

SOLUTION: This exhaust emission control device for an internal combustion engine having the storage and reduction type NOx catalyst 17 in an exhaust pipe 16 for the lean-combustible internal combustion engine comprises an incoming gas SOx sensor 23 provided at the upstream side of the NOx catalyst 17 and an outgoing gas SOx sensor 24 and an air/fuel ratio sensor 27 at the downstream side. SOx poisoning recovery treatment is executed to the NOx catalyst 17, and right after almost complete poisoning recovery, saturated NOx release treatment is executed to the NOx catalyst 17 and a change-to-rich time is measured and compared with a change-to-rich time for a new NOx catalyst 17 for judging the degree of thermal deterioration in accordance with the comparison value. Otherwise, the NOx clean-up rate of the NOx catalyst is measured for judging the degree of thermal deterioration. When the degree of thermal deterioration exceeds a preset level, thermal deterioration inhibiting means is operated for inhibiting further thermal deterioration.



BEST AVAILABLE COPY

LEGAL STATUS

[Date of request for examination]

20.06.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] (b) The occlusion reduction type NOx catalyst which emits NOx absorbed when the oxygen density of the exhaust gas which is formed in the flueway of the internal combustion engine in which lean combustion is possible, absorbs NOx and flows when the air-fuel ratio of the flowing exhaust gas is Lean was low, and returns to N2, (**), when judged with it being an activation stage by poisoning recovery activation stage judging means to perform SOx poisoning recovery to which SOx is made to emit from said occlusion reduction type NOx catalyst and to judge whether it is a stage, and said (Ha) poisoning recovery activation stage judging means SOx deposited on said occlusion reduction type NOx catalyst -- the whole quantity is emitted mostly -- making -- this occlusion reduction type NOx catalyst -- SOx With a poisoning recovery means to recover poisoning (d) An occlusion capacity detection means to detect the NOx occlusion capacity of said occlusion reduction type NOx catalyst, (e) The NOx occlusion capacity it is incapable on the NOx occlusion capacity of said occlusion reduction type NOx catalyst detected by said occlusion capacity detection means after performing SOx poisoning recovery with said poisoning recovery means, and criteria is measured. The exhaust emission control device of the internal combustion engine characterized by having a heat deterioration judging means to judge the heat deterioration degree of this occlusion reduction type NOx catalyst based on the compound value.

[Claim 2] Said occlusion capacity detection means is the exhaust emission control device of the internal combustion engine according to claim 1 characterized by using as the barometer of NOx occlusion capacity a duration after making the NOx occlusion condition of an occlusion reduction type NOx catalyst into a saturation state, until it changes the air-fuel ratio of the exhaust gas which flows into this occlusion reduction type NOx catalyst to Ricci from Lean, it maintains to Ricci and the air-fuel ratio of the exhaust gas of the outlet of this occlusion reduction type NOx catalyst becomes Ricci from the change of this air-fuel ratio.

[Claim 3] Said poisoning recovery activation stage judging means is the exhaust emission control device of the internal combustion engine according to claim 1 or 2 characterized by judging with it being the activation stage of SOx poisoning recovery when the NOx occlusion capacity of the occlusion reduction type NOx catalyst detected by said occlusion capacity detection means is less than a predetermined lower limit.

[Claim 4] (b) The occlusion reduction type NOx catalyst which emits NOx absorbed when the oxygen density of the exhaust gas which is formed in the flueway of the internal combustion engine in which lean combustion is possible, absorbs NOx and flows when the air-fuel ratio of the flowing exhaust gas is Lean was low, and returns to N2, (**), when judged with it being an activation stage by poisoning recovery activation stage judging means to perform SOx poisoning recovery to which SOx is made to emit from said occlusion reduction type NOx catalyst and to judge whether it is a stage, and said (Ha) poisoning recovery activation stage judging means SOx deposited on said occlusion reduction type NOx catalyst -- the whole quantity is emitted mostly -- making -- this occlusion reduction type NOx catalyst -- SOx With a poisoning recovery means to recover poisoning (d) A rate measurement means of clarification to measure the rate of NOx clarification of said occlusion reduction type NOx catalyst, (e) The rate of NOx clarification used as the rate criteria of NOx clarification of said occlusion reduction type NOx catalyst measured by said rate measurement of clarification after performing SOx poisoning recovery with said poisoning recovery means is compared. The exhaust emission control device of the internal combustion engine characterized by having a heat deterioration judging means to judge the heat deterioration degree of this occlusion reduction type NOx catalyst based on the compound value.

[Claim 5] Said rate measurement means of NOx clarification is the exhaust emission control device of the

internal combustion engine according to claim 3 or 2 characterized by measuring the rate of NO_x clarification based on the amount of NO_x in the exhaust gas which flows into a NO_x catalyst, and the amount of NO_x in the exhaust gas by the NO_x detection means installed in the lower stream of a river of a NO_x catalyst.

[Claim 6] Said poisoning recovery activation stage judging means is the exhaust emission control device of the internal combustion engine according to claim 3 or 4 characterized by judging with it being the activation stage of SO_x poisoning recovery when the rate of NO_x clarification of the occlusion reduction type NO_x catalyst measured by said rate measurement means of clarification is less than a predetermined lower limit.

[Claim 7] It has a close gas SO_x concentration detection means to detect the SO_x concentration of the exhaust gas which flows into said occlusion reduction type NO_x catalyst. Said poisoning recovery activation stage judging means When the SO_x concentration detected by said close gas SO_x concentration detection means and the amount of SO_x which flows into the occlusion reduction type NO_x catalyst computed based on said internal combustion engine's inhalation air content exceed the specified quantity The exhaust emission control device of an internal combustion engine given in either of claims 1-6 characterized by judging with it being the activation stage of SO_x poisoning recovery.

[Claim 8] It has a close gas SO_x concentration detection means to detect the SO_x concentration of the exhaust gas which flows into said occlusion reduction type NO_x catalyst. Said poisoning recovery activation stage judging means When the amount of SO_x which flows into the occlusion reduction type NO_x catalyst computed based on the sulfur concentration, fuel consumption, or mileage of a fuel of said internal combustion engine which presumed from the SO_x concentration detected by said close gas SO_x concentration detection means exceeds the specified quantity The exhaust emission control device of an internal combustion engine given in either of claims 1-6 characterized by judging with it being the activation stage of SO_x poisoning recovery.

[Claim 9] A close gas SO_x concentration detection means to detect the SO_x concentration of the exhaust gas which flows into said occlusion reduction type NO_x catalyst, It has an appearance gas SO_x concentration detection means to detect the SO_x concentration of the exhaust gas which flows out of this occlusion reduction type NO_x catalyst. Said poisoning recovery activation stage judging means When the amount of SO_x occlusion presumed based on inhalation air content or amount of exhaust gas of the concentration difference of the SO_x concentration detected by said close gas SO_x concentration detection means and the SO_x concentration detected by said appearance gas SO_x concentration detection means and said internal combustion engine exceeds the specified quantity The exhaust emission control device of an internal combustion engine given in either of claims 1-6 characterized by judging with it being the activation stage of SO_x poisoning recovery.

[Claim 10] A close gas SO_x concentration detection means to detect the SO_x concentration of the exhaust gas which flows into said occlusion reduction type NO_x catalyst, It has an appearance gas SO_x concentration detection means to detect the SO_x concentration of the exhaust gas which flows out of this occlusion reduction type NO_x catalyst. Said poisoning recovery activation stage judging means When it approaches to predetermined level to the SO_x concentration by which the SO_x concentration detected by said appearance gas SO_x concentration detection means was detected by said close gas SO_x concentration detection means The exhaust emission control device of an internal combustion engine given in either of claims 1-6 characterized by judging with it being the activation stage of SO_x poisoning recovery.

[Claim 11] From the amount of SO_x occlusion presumed that occlusion was carried out to said occlusion reduction type NO_x catalyst It is SO_x by said poisoning recovery means. When performing poisoning recovery The amount of bleedoff SO_x presumed based on inhalation air content or amount of exhaust gas of the concentration difference of the SO_x concentration detected by the ***** gas SO_x concentration detection means and the SO_x concentration detected by said close gas SO_x concentration detection means and said internal combustion engine is subtracted. SO_x by said poisoning recovery means when the amount of SO_x which remains for an occlusion reduction type NO_x catalyst is presumed and this SO_x ullage decreases to the specified quantity Exhaust emission control device of the internal combustion engine according to claim 9 characterized by ending poisoning recovery.

[Claim 12] It is the exhaust emission control device of an internal combustion engine given in either of claims 1-6 characterized by having a heat deterioration control means to control the heat deterioration of said occlusion reduction type NO_x catalyst, for this heat deterioration control means not operating when the heat deterioration degree judged by said heat deterioration judging means is below predetermined level, but operating when said predetermined level is exceeded.

[Claim 13] Said heat deterioration control means is the exhaust emission control device of the internal combustion engine according to claim 12 characterized by being the fuel cut prohibition control which forbids a fuel cut in an internal combustion engine's elevated-temperature operation region.

[Claim 14] Said heat deterioration control means is the exhaust emission control device of the internal combustion engine according to claim 12 characterized by being the Lean operating-range reduction control which decreases a Lean operating range in an internal combustion engine's elevated-temperature operation region.

[Claim 15] Ricci who makes it flow into a NOx catalyst according to the degree of heat deterioration, or the amount of exhaust gas of SUTOIKI is increased, or said heat deterioration control means is /. And exhaust emission control device of the internal combustion engine according to claim 12 characterized by shortening the period which makes the exhaust gas of Ricci or SUTOIKI flow into a NOx catalyst.

[Translation done.]

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to what can start the exhaust emission control device which can purify nitrogen oxides (NOx) from the exhaust gas discharged by the internal combustion engine in which lean combustion is possible, especially can detect the heat deterioration of a NOx catalyst.

[0002]

[Description of the Prior Art] There is an occlusion reduction type NOx catalyst as an exhaust emission control device which purifies NOx from the exhaust gas discharged by the internal combustion engine in which lean combustion is possible. An occlusion reduction type NOx catalyst (it may only be hereafter called a catalyst or a NOx catalyst) is a catalyst which emits NOx which absorbed NOx when the air-fuel ratio of inflow exhaust gas was Lean (namely, under a hyperoxia ambient atmosphere), and was absorbed when the oxygen density of inflow exhaust gas fell, and returns to N2.

[0003] When the structure of a NOx catalyst and the mechanism of NOx clarification are explained briefly, a NOx catalyst It comes to **** NOx occlusion agents, such as catalyst matter, such as platinum (Pt), and barium (Ba), on support, such as an alumina, (in the following explanation). If the exhaust gas of the Lean air-fuel ratio flows into the NOx catalyst explained in the example of the NOx catalyst which comes to **** Pt and Ba, NOx in exhaust gas oxidizes on the surface of Pt, is set to NO2, this NO2 will be absorbed in Ba, and will combine with BaO and will be absorbed in the form of nitrate ion NO3-. Absorption of this NOx is performed in the interface of Ba and Pt. On the other hand, when the exhaust gas of SUTOIKI (theoretical air fuel ratio) or the Ricci air-fuel ratio flows into a NOx catalyst and an oxygen density falls, NO3- absorbed by the NOx catalyst is emitted in the form of NO2 or NO, reacts with HC in exhaust gas, and CO further, and is made to return to N2.

[0004] Therefore, if this NOx catalyst is arranged to the flueway of the internal combustion engine in which lean combustion is possible and the exhaust gas of the Lean air-fuel ratio and the exhaust gas of SUTOIKI or the Ricci air-fuel ratio are passed by turns, NOx in exhaust gas can be purified.

[0005] If this NOx catalyst is used for exhaust gas clarification at the long period of time, this NOx catalyst carries out degradation with the passage of time, and it is known that NOx clarification capacity will decline as shown in drawing 5. It is thought that this degradation has a cause in the sulfur in the (a) fuel and (b) heat, degradation resulting from the sulfur in a fuel may be called sulfur poisoning degradation, degradation resulting from heat may be called heat deterioration, and it may distinguish. In addition, although sulfur poisoning degradation may be expressed as S poisoning degradation or SOx poisoning degradation, it is unified with an expression called SOx poisoning degradation by the following explanation.

[0006] If SOx poisoning degradation is explained, generally sulfur content is contained in the fuel for an internal combustion engine, if a fuel is burned with an internal combustion engine, the sulfur content in a fuel will burn and sulfur oxides (SOx), such as SO2 and SO3, will be generated. Since said occlusion reduction type NOx catalyst absorbs SOx in exhaust gas by the same mechanism as performing absorption of NOx, if a NOx catalyst is arranged to an internal combustion engine's flueway, not only NOx but SOx will be absorbed by this NOx catalyst.

[0007] However, SOx absorbed by said NOx catalyst is easy to tend be accumulated into a catalyst that it decomposes and is hard to be emitted in order to form a stable sulfate with time amount progress. It is called SOx poisoning that a sulfate is accumulated in a NOx catalyst, and if SOx poisoning advances and the SOx accumulated dose within a NOx catalyst increases, in order that the NOx absorption capacity of a catalyst may decrease, the rate of NOx clarification will fall. This is SOx poisoning degradation.

[0008] Although absorption of NOx in a NOx catalyst will be performed in the interface of Pt (catalyst

matter) and Ba (NO_x absorbent) as mentioned above if heat deterioration is explained, as for Pt, it is known in sintering by heat a lifting and that will grow up and particle size will become large. In clarification of the exhaust gas discharged by the internal combustion engine for cars, the thermal load which joins a NO_x catalyst is large, and sintering of Pt cannot be avoided. Thus, if Pt causes sintering, the touch area of Pt and Ba will decrease, namely, the interface of Pt and Ba will decrease. Consequently, the NO_x absorptance of a NO_x catalyst declines and NO_x clarification capacity declines. This is heat deterioration.

[0009] while sintering (particle-size growth of the catalyst matter) of the catalyst matter shows the effect which it has on the NO_x clarification engine performance and sintering of the catalyst matter is not progressing, the NO_x clarification engine performance of drawing 12 is high (namely, when particle size is small), and sintering progresses -- it is alike, and it follows and the NO_x (that is, particle size becomes large -- alike -- following) clarification engine performance falls.

[0010]

[Problem(s) to be Solved by the Invention] By the way, since SO_x absorbed by the NO_x catalyst by performing predetermined recovery can be made to be able to emit and it can return to SO₂ about said SO_x poisoning degradation as indicated by the patent official report of a patent number No. 2745985 etc., it is possible to recover a NO_x catalyst from SO_x poisoning.

[0011] On the other hand, it is impossible to return to the condition before carrying out sintering of the Pt which caused sintering once, therefore it is impossible to recover a NO_x catalyst from heat deterioration. Therefore, detecting the degree (heat deterioration level) of the heat deterioration of a NO_x catalyst, when managing a NO_x catalyst has important semantics.

[0012] However, the technique of now detecting a heat deterioration degree is not established, but it is anxious for development of the technique of detecting the degree of heat deterioration. This invention is made in view of the trouble of such a Prior art, and the technical problem which this invention tends to solve is shown in aiming at improvement in an internal combustion engine's exhaust air clarification technique by establishing the detection technique of the heat deterioration degree of an occlusion reduction type NO_x catalyst.

[0013]

[Means for Solving the Problem] This invention adopted the following means, in order to solve said technical problem. The exhaust emission control device of the internal combustion engine concerning the 1st invention The occlusion reduction type NO_x catalyst which emits NO_x absorbed when the oxygen density of the exhaust gas which is formed in the flueway of the internal combustion engine in which (b) lean combustion is possible, absorbs NO_x and flows when the air-fuel ratio of the flowing exhaust gas is Lean was low, and returns to N₂, (**), when judged with it being an activation stage by poisoning recovery activation stage judging means to perform SO_x poisoning recovery to which SO_x is made to emit from said occlusion reduction type NO_x catalyst and to judge whether it is a stage, and said (Ha) poisoning recovery activation stage judging means SO_x deposited on said occlusion reduction type NO_x catalyst -- the whole quantity is emitted mostly -- making -- this occlusion reduction type NO_x catalyst -- SO_x With a poisoning recovery means to recover poisoning (d) An occlusion capacity detection means to detect the NO_x occlusion capacity of said occlusion reduction type NO_x catalyst, (e) The NO_x occlusion capacity it is incapable on the NO_x occlusion capacity of said occlusion reduction type NO_x catalyst detected by said occlusion capacity detection means after performing SO_x poisoning recovery with said poisoning recovery means, and criteria is measured. It is characterized by having a heat deterioration judging means to judge the heat deterioration degree of this occlusion reduction type NO_x catalyst based on the compound value.

[0014] In this internal combustion engine's exhaust emission control device, if it judges with a poisoning recovery activation stage judging means being the stage when SO_x poisoning recovery should be performed to an occlusion reduction type NO_x catalyst, a poisoning recovery means will perform SO_x poisoning recovery to an occlusion reduction type NO_x catalyst, and will emit nearly thoroughly SO_x by which occlusion is carried out to the occlusion reduction type NO_x catalyst. And an occlusion capacity detection means detects the NO_x occlusion capacity of an occlusion reduction type NO_x catalyst immediately after completion of SO_x poisoning recovery. Then, the NO_x occlusion capacity for a heat deterioration judging means to serve as NO_x occlusion capacity detected by the occlusion capacity detection means and criteria is measured, and the heat deterioration degree of an occlusion reduction type NO_x catalyst is judged based on that compound value.

[0015] The judgment principle of a heat deterioration degree is as follows. Although there are SO_x poisoning degradation resulting from the sulfur in a fuel and heat deterioration resulting from heat in degradation of an occlusion reduction type NO_x catalyst, heat deterioration is unrecoverable to SO_x

poisoning degradation being recoverable if predetermined poisoning recovery is performed, once it is generated. Therefore, even if it performs SOx poisoning recovery, it can be considered that still an engine-performance unrecoverable part is what is depended on heat deterioration. This is the principle of the heat deterioration degree judging in this invention.

[0016] In the exhaust emission control device of the internal combustion engine concerning the 1st invention, NOx occlusion capacity which said heat deterioration judging means makes criteria can be made into the NOx occlusion capacity of a new occlusion reduction type NOx catalyst to have received neither SOx poisoning degradation nor heat deterioration.

[0017] The compound value which measures and searches for the NOx occlusion capacity for said heat deterioration judging means to serve as NOx occlusion capacity of said occlusion reduction type NOx catalyst detected by said occlusion capacity detection means and criteria is good also as both difference, and good also as a quotient which $\frac{a}{b}$ (ed) one side on the other hand.

[0018] Moreover, the exhaust emission control device of the internal combustion engine concerning the 2nd invention The occlusion reduction type NOx catalyst which emits NOx absorbed when the oxygen density of the exhaust gas which is formed in the flueway of the internal combustion engine in which (b) lean combustion is possible, absorbs NOx and flows when the air-fuel ratio of the flowing exhaust gas is Lean was low, and returns to N2, $\frac{a}{b}$), when judged with it being an activation stage by poisoning recovery activation stage judging means to perform SOx poisoning recovery to which SOx is made to emit from said occlusion reduction type NOx catalyst and to judge whether it is a stage, and said (Ha) poisoning recovery activation stage judging means SOx deposited on said occlusion reduction type NOx catalyst -- the whole quantity is emitted mostly -- making -- this occlusion reduction type NOx catalyst -- SOx With a poisoning recovery means to recover poisoning (d) A rate measurement means of clarification to measure the rate of NOx clarification of said occlusion reduction type NOx catalyst, (e) The rate of NOx clarification used as the rate criteria of NOx clarification of said occlusion reduction type NOx catalyst measured by said rate measurement of clarification after performing SOx poisoning recovery with said poisoning recovery means is compared. [0019] characterized by having a heat deterioration judging means to judge the heat deterioration degree of this occlusion reduction type NOx catalyst based on the compound value In the 2nd invention, said rate measurement means of NOx clarification can measure the rate of NOx clarification based on the amount of NOx in the exhaust gas which flows into a NOx catalyst, and the amount of NOx in the exhaust gas by the NOx detection means installed in the lower stream of a river of a NOx catalyst. In the exhaust emission control device of the internal combustion engine of the 2nd invention, if it judges with a poisoning recovery activation stage judging means being the stage when SOx poisoning recovery should be performed to an occlusion reduction type NOx catalyst, a poisoning recovery means will perform SOx poisoning recovery to an occlusion reduction type NOx catalyst, and will emit nearly thoroughly SOx by which occlusion is carried out to the occlusion reduction type NOx catalyst. And the rate measurement means of clarification measures the rate of NOx clarification of an occlusion reduction type NOx catalyst immediately after completion of SOx poisoning recovery. Then, the rate of NOx clarification from which a heat deterioration judging means serves as a rate of NOx clarification measured by the rate measurement means of clarification and criteria is compared, and the heat deterioration degree of an occlusion reduction type NOx catalyst is judged based on that compound value.

[0020] The judgment principle of a heat deterioration degree is as follows. Although there are SOx poisoning degradation resulting from the sulfur in a fuel and heat deterioration resulting from heat in degradation of an occlusion reduction type NOx catalyst, heat deterioration is unrecoverable to SOx poisoning degradation being recoverable if predetermined poisoning recovery is performed, once it is generated. Therefore, even if it performs SOx poisoning recovery, it can be considered that still an engine-performance unrecoverable part is what is depended on heat deterioration. This is the principle of the heat deterioration degree judging in this invention.

[0021] In the exhaust emission control device of the internal combustion engine concerning the 2nd invention, the rate of NOx clarification which said heat deterioration judging means makes criteria can be made into the rate of NOx clarification of the occlusion reduction type NOx catalyst of the new article which has received neither SOx poisoning degradation nor heat deterioration.

[0022] The compound value which compares and asks for the rate of NOx clarification from which said heat deterioration judging means serves as a rate of NOx clarification of said occlusion reduction type NOx catalyst measured by said rate measurement means of clarification and criteria is good also as both difference, and good also as a quotient which $\frac{a}{b}$ (ed) one side on the other hand.

[0023] As an internal combustion engine in the 1st and 2nd invention (following, this invention) in which

lean combustion is possible, the lean burn gasoline engine and diesel power plant of the direct injection in a cylinder can be illustrated. The air-fuel ratio of exhaust gas means the ratio of the air supplied in the flueway in the upstream rather than the engine inhalation-of-air path and the occlusion reduction type NOx catalyst, and a fuel (hydrocarbon).

[0024] When an internal combustion engine is a lean burn gasoline engine, an exhaust air Air Fuel Ratio Control means can control the air-fuel ratio of exhaust gas by controlling the air-fuel ratio of the gaseous mixture supplied to a combustion chamber. Moreover, when an internal combustion engine is a diesel power plant, the air-fuel ratio of exhaust gas can be controlled the so-called subinjection which injects a fuel by the intake stroke, the expansion stroke, or the exhaust stroke, or by supplying a reducing agent in an upstream flueway rather than an occlusion reduction type NOx catalyst.

[0025] An occlusion reduction type NOx catalyst is a catalyst which emits NOx absorbed when the air-fuel ratio of the flowing exhaust gas was Lean, NOx was absorbed and the oxygen density in the flowing exhaust gas fell, and returns to N₂. This occlusion reduction type NOx catalyst makes an alumina support, and it comes to support at least one chosen from Potassium K, Sodium Na, Lithium Li, alkali metal like Caesium Cs, Barium Ba, an alkaline earth like Calcium calcium, Lanthanum La, and rare earth like Yttrium Y, and noble metals like Platinum Pt on this support.

[0026] Moreover, after said occlusion capacity detection means makes a saturation state the NOx occlusion condition of an occlusion reduction type NOx catalyst, it can change the air-fuel ratio of the exhaust gas which flows into this occlusion reduction type NOx catalyst to Ricci from Lean, can be maintained to Ricci, and can detect a duration until the air-fuel ratio of the exhaust gas of the outlet of this occlusion reduction type NOx catalyst becomes Ricci from the change of this air-fuel ratio as a barometer of NOx occlusion capacity.

[0027] In the exhaust emission control device of the internal combustion engine concerning this invention, it can judge with said poisoning recovery activation stage judging means being the activation stage of SOx poisoning recovery, when the NOx occlusion capacity of the occlusion reduction type NOx catalyst detected by said occlusion capacity detection means is less than a predetermined lower limit. In this case, it is desirable that an occlusion capacity detection means detects the NOx occlusion capacity of an occlusion reduction type NOx catalyst for every fixed fuel consumption and every fixed mileage, for example.

[0028] Moreover, it can have a close gas SOx concentration detection means detect the SOx concentration of the exhaust gas which flows into said occlusion reduction type NOx catalyst, and it can judge with said poisoning recovery activation stage judging means being the activation stage of SOx poisoning recovery, when the SOx concentration detected by said close gas SOx concentration detection means and the amount of SOx which flows into the occlusion reduction type NOx catalyst computed based on said internal combustion engine's inhalation air content exceed the specified quantity.

[0029] It has a close gas SOx concentration detection means to detect the SOx concentration of the exhaust gas which furthermore flows into said occlusion reduction type NOx catalyst. Said poisoning recovery activation stage judging means When the amount of SOx which flows into the occlusion reduction type NOx catalyst computed based on the sulfur concentration, fuel consumption, or mileage of a fuel of said internal combustion engine which presumed from the SOx concentration detected by said close gas SOx concentration detection means exceeds the specified quantity It can judge with it being the activation stage of SOx poisoning recovery. Also when are done in this way and the fuel with which sulfur concentration differs is used, a heat deterioration degree can be judged.

[0030] In the exhaust emission control device of the internal combustion engine concerning this invention A close gas SOx concentration detection means to detect the SOx concentration of the exhaust gas which flows into said occlusion reduction type NOx catalyst, It has an appearance gas SOx concentration detection means to detect the SOx concentration of the exhaust gas which flows out of this occlusion reduction type NOx catalyst. Said poisoning recovery activation stage judging means When the amount of SOx occlusion presumed based on inhalation air content or amount of exhaust gas of the concentration difference of the SOx concentration detected by said close gas SOx concentration detection means and the SOx concentration detected by said appearance gas SOx concentration detection means and said internal combustion engine exceeds the specified quantity It can judge with it being the activation stage of SOx poisoning recovery. case the SOx concentration of the upstream of an occlusion reduction type NOx catalyst is larger than the SOx concentration of the lower stream of a river of an occlusion reduction type NOx catalyst -- the concentration -- it is because it is possible that difference is absorbed by the occlusion reduction type NOx catalyst.

[0031] A close gas SOx concentration detection means to detect the SOx concentration of the exhaust gas which flows into said occlusion reduction type NOx catalyst, It has an appearance gas SOx concentration

detection means to detect the SOx concentration of the exhaust gas which flows out of this occlusion reduction type NOx catalyst. Said poisoning recovery activation stage judging means When it approaches to predetermined level to the SOx concentration by which the SOx concentration detected by said appearance gas SOx concentration detection means was detected by said close gas SOx concentration detection means, it can judge with it being the activation stage of SOx poisoning recovery. It is because the SOx concentration of the lower stream of a river of an occlusion reduction type NOx catalyst approaches the SOx concentration of the upstream of an occlusion reduction type NOx catalyst as the SOx accumulated dose of an occlusion reduction type NOx catalyst approaches a saturation state.

[0032] When it comes out with said close gas SOx concentration detection means and has a gas SOx concentration detection means in the exhaust emission control device of the internal combustion engine concerning this invention From the amount of SOx occlusion presumed that occlusion was carried out to said occlusion reduction type NOx catalyst It is SOx by said poisoning recovery means. When performing poisoning recovery The amount of bleedoff SOx presumed based on inhalation air content or amount of exhaust gas of the concentration difference of the SOx concentration detected by the ***** gas SOx concentration detection means and the SOx concentration detected by said close gas SOx concentration detection means and said internal combustion engine is subtracted. SOx by said poisoning recovery means when the amount of SOx which remains for an occlusion reduction type NOx catalyst is presumed and this SOx ullage decreases to the specified quantity Poisoning recovery can be ended. case the SOx concentration of the lower stream of a river of an occlusion reduction type NOx catalyst is larger than the SOx concentration of the upstream of an occlusion reduction type NOx catalyst -- the concentration -- difference is SOx emitted from the occlusion reduction type NOx catalyst -- it is because it can think and calculation presumption of the amount of bleedoff SOx can be carried out based on this, an inhalation air content, or the amount of exhaust gas.

[0033] In the exhaust emission control device of the internal combustion engine concerning this invention, it has a heat deterioration control means to control the heat deterioration of said occlusion reduction type NOx catalyst, and when the heat deterioration degree judged by said heat deterioration judging means is below predetermined level, it does not operate, but this heat deterioration control means can operate, when said predetermined level is exceeded. It can control by this that heat deterioration advances more than it, and lowering of the NOx occlusion capacity of an occlusion reduction type NOx catalyst can be controlled.

[0034] In the exhaust emission control device of the internal combustion engine concerning this invention, said heat deterioration control means can be considered as the fuel cut prohibition control which forbids a fuel cut in an internal combustion engine's elevated-temperature operation region. If a fuel cut is performed in an elevated-temperature operation region, when a hot occlusion reduction type NOx catalyst is in an elevated-temperature condition, the high exhaust gas of an oxygen density will be passed, and sintering of the catalyst matter which caused heat deterioration will be promoted. This can be prevented if a fuel cut in an elevated-temperature operation region is forbidden.

[0035] In the exhaust emission control device of the internal combustion engine concerning this invention, said heat deterioration control means can consider a Lean operating range in an internal combustion engine's elevated-temperature operation region as the Lean operating-range reduction control which decreases. By decreasing a Lean operating range in an elevated-temperature operation region, it can decrease that the high exhaust gas of an oxygen density flows for an occlusion reduction type NOx catalyst in an elevated-temperature operation region, consequently the heat deterioration of an occlusion reduction type NOx catalyst can be controlled. Furthermore, said heat deterioration control means can be considered as the Ricci Spike control which shortens the period which increases Ricci who flows into a NOx catalyst according to the degree of heat deterioration, or the amount of exhaust gas of SUTOIKI, or/and makes the exhaust gas of Ricci or SUTOIKI flow into a NOx catalyst. Thus, the amount of the reducing agent for carrying out bleedoff of NOx and reduction according to extent of heat deterioration can be made [many], and operation ***** by the heat deterioration of an occlusion reduction type NOx catalyst can be controlled.

[0036]

[Embodiment of the Invention] Hereafter, the gestalt of operation of the exhaust emission control device of the internal combustion engine concerning this invention is explained based on the drawing of drawing 11 from drawing 1.

[0037] [Gestalt of the 1st operation] Drawing 1 is drawing showing the outline configuration at the time of applying this invention to the gasoline engine for cars in which lean combustion is possible. this drawing -- setting -- a sign 1 -- an engine body and a sign 2 -- a piston and a sign 3 -- in an inlet valve and a sign 6, an inlet port and a sign 7 show an exhaust valve, and, as for a combustion chamber and a sign 4, a sign 8 shows

[an ignition plug and a sign 5] an exhaust port, respectively.

[0038] An inlet port 6 is connected with a surge tank 10 through the corresponding branch pipe 9, and the fuel injection valve 11 which injects a fuel towards the inside of an inlet port 6, respectively is attached in each branch pipe 9. A surge tank 10 is connected with an air cleaner 13 through an air intake duct 12 and an air flow meter 21, and the throttle valve 14 is arranged in the air intake duct 12.

[0039] On the other hand, an exhaust port 8 is connected to the casing 18 which built in the occlusion reduction type NOx catalyst 17 (it may abbreviate to a NOx catalyst in the following explanation) through the exhaust manifold 15 and the exhaust pipe 16, and casing 18 is connected to the muffler which is not illustrated through an exhaust pipe 19.

[0040] The electronic control unit (ECU) 30 for engine control consists of a digital computer, and ROM (read-only memory)32, RAM (random access memory)33, CPU (central processor unit)34, the input port 35, and the output port 36 which were mutually connected by the bi-directional bus 31 are provided. An air flow meter 21 generates the output voltage proportional to an inhalation air content, and this output voltage is inputted into input port 35 through A-D converter 38.

[0041] The close gas SOx sensor (close gas SOx concentration detection means) 23 which generates the output voltage proportional to the SOx concentration of the exhaust gas (this is hereafter called close gas) which flows into the NOx catalyst 17 is formed in the exhaust pipe 16 of the upstream of casing 18. On the other hand, the appearance gas SOx sensor (appearance gas SOx concentration detection means) 24 which generates the output voltage proportional to the SOx concentration of the exhaust gas (henceforth [it comes out of this and] gas) which flows out of the NOx catalyst 17, the temperature sensor 25 which generates the output voltage proportional to the temperature of appearance gas, and the air-fuel ratio sensor 27 which generates the output voltage showing the air-fuel ratio of appearance gas are attached in the exhaust pipe 19 of the lower stream of a river of casing 18. The output voltage of these SOx sensors 23 and 24, a temperature sensor 25, and the air-fuel ratio sensor 27 is inputted into input port 35 through corresponding A-D converter 38, respectively.

[0042] Moreover, the rotational frequency sensor 26 which generates the output pulse showing an engine rotational frequency is connected to input port 35. The output port 36 is connected to the ignition plug 4 and the fuel injection valve 11 through the corresponding actuation circuit 39, respectively.

[0043] In this gasoline engine, fuel injection duration TAU is computed, for example based on a degree type.

TAU=TP-K -- here, TP shows basic fuel injection duration and K shows the correction factor. The basic fuel injection duration TP shows fuel injection duration required to make into theoretical air fuel ratio the air-fuel ratio of the gaseous mixture supplied in an engine cylinder. This basic fuel injection duration TP is beforehand found by experiment, and is beforehand memorized in ROM32 in the form of a map as shown in drawing 2 as a function of engine load Q/N (inhalation air content Q / engine rotational frequency N) and the engine rotational frequency N. A correction factor K is a multiplier for controlling the air-fuel ratio of the gaseous mixture supplied in an engine cylinder, and if it is K= 1.0, the gaseous mixture supplied in an engine cylinder will serve as theoretical air fuel ratio. On the other hand, if the air-fuel ratio of the gaseous mixture supplied in an engine cylinder will become larger than theoretical air fuel ratio if set to K< 1.0, namely, it becomes Lean and it is set to K> 1.0, the air-fuel ratio of the gaseous mixture supplied in an engine cylinder will become smaller than theoretical air fuel ratio, namely, will serve as Ricci.

[0044] and in the gasoline engine of the gestalt of this operation Lean Air Fuel Ratio Control is performed the value of a correction factor K being used as a value smaller than 1.0 in a load operating range in engine low. At the time of the warm-up at the time of an engine heavy load operating range and engine start up, at the time of acceleration, SUTOIKI control is performed the value of a correction factor K being used as 1.0, and by the time of high-speed fixed-speed operation, by the engine full load operating range, the value of a correction factor K is set up so that it may consider as a bigger value than 1.0 and Ricci Air Fuel Ratio Control may be performed.

[0045] in an internal combustion engine, the value of a correction factor K usually makes [in / the frequency by which load operation in low is carried out is the highest, therefore / most in an operating period] it smaller than 1.0 -- having -- Lean -- gaseous mixture is made to burn

[0046] Drawing 3 shows roughly the concentration of the typical component in the exhaust gas discharged from a combustion chamber 3. unburnt [in the exhaust gas discharged from a combustion chamber 3 as shown in this drawing] -- the concentration of HC and CO increases, so that the air-fuel ratio of the gaseous mixture supplied in a combustion chamber 3 becomes Ricci, and the concentration of the oxygen O2 in the exhaust gas discharged from a combustion chamber 3 increases, so that the air-fuel ratio of the gaseous

mixture supplied in a combustion chamber 3 becomes Lean.

[0047] The NOx catalyst (occlusion reduction type NOx catalyst) 17 held in casing 18 makes an alumina support, and it comes to support at least one chosen from Potassium K, Sodium Na, Lithium Li, alkali metal like Caesium Cs, Barium Ba, an alkaline earth like Calcium calcium, Lanthanum La, and rare earth like Yttrium Y, and noble metals like Platinum Pt on this support.

[0048] The absorption/emission action of NOx which emits NOx absorbed when the NOx catalyst 17 absorbed NOx when the air-fuel ratio (it may be hereafter called an exhaust air air-fuel ratio) of the flowing exhaust gas was Lean when this NOx catalyst 17 had been arranged to an engine's flueway, and the oxygen density in inflow exhaust gas fell is performed. Here, an exhaust air air-fuel ratio means the ratio of the air supplied in the upstream flueway from the engine inhalation-of-air path and the NOx catalyst 17, and a fuel (hydrocarbon).

[0049] in addition, when a fuel (hydrocarbon) or air is not supplied in an upstream flueway from the NOx catalyst 17 An exhaust air air-fuel ratio is [therefore] in agreement with the air-fuel ratio of the gaseous mixture supplied in a combustion chamber 3. In this case the gaseous mixture which the NOx catalyst 17 absorbs NOx when the air-fuel ratio of the gaseous mixture supplied in a combustion chamber 3 is Lean, and is supplied in a combustion chamber 3 -- NOx absorbed when the inner oxygen density fell will be emitted.

[0050] It is thought that the absorption/emission action of NOx by the NOx catalyst 17 is performed by the mechanism as shown in drawing 4 . Although this mechanism is hereafter explained taking the case of the case where Platinum Pt and Barium Ba are made to support, on support, it becomes the same mechanism even if it uses other noble metals, alkali metal, an alkaline earth, and rare earth.

[0051] First, as the oxygen density in inflow exhaust gas will increase sharply if inflow exhaust gas becomes Lean considerably, and shown in drawing 4 (A), it is oxygen O2. It adheres to the front face of Platinum Pt in the form of O2- or O2-. On the other hand, NO contained in inflow exhaust gas reacts with O2- or O2- on the front face of Platinum Pt, and is NO2. It becomes ($2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$).

[0052] Subsequently, being absorbed in Ba and combining with the barium oxide BaO oxidizing on Platinum Pt, a part of generated NO2 is diffused in Ba in the form of nitrate ion NO3-, as shown in drawing 4 (A). Thus, NOx is absorbed in the NOx catalyst 17.

[0053] As long as the oxygen density in inflow exhaust gas is high, NO2 is generated on the front face of Platinum Pt, and it is NOx of the NOx catalyst 17. Unless absorptance is saturated, NO2 is absorbed in the NOx catalyst 17, and nitrate ion NO3- is generated.

[0054] On the other hand, if the oxygen density in inflow exhaust gas falls and the amount of generation of NO2 falls, a reaction will go to hard flow ($\text{NO}_3^- \rightarrow \text{NO}_2$), and nitrate ion NO3- in Ba will be emitted from Ba in the form of NO2 or NO. That is, lowering of the oxygen density in inflow exhaust gas will emit NOx from the NOx catalyst 17. If the oxygen density in inflow exhaust gas will fall if the degree of Lean of inflow exhaust gas becomes low, therefore the degree of Lean of inflow exhaust gas is made low as shown in drawing 3 , NOx will be emitted from the NOx catalyst 17.

[0055] on the other hand, when the gaseous mixture supplied in a combustion chamber 3 becomes SUTOIKI or the Ricci air-fuel ratio at this time, it is shown in drawing 3 -- as -- unburnt [from an engine / a lot of] -- HC and CO discharge -- having -- unburnt [these] -- HC and CO react with oxygen O2- on Platinum Pt, or O2-, and are made to oxidize

[0056] moreover, if an exhaust air air-fuel ratio turns into theoretical air fuel ratio or the Ricci air-fuel ratio, in order for the oxygen density in inflow exhaust gas to fall to the degree of pole, NO2 or NO is emitted from the NOx catalyst 17, and this NO2 or NO is shown in drawing 4 (B) -- as -- unburnt -- it reacts with HC and CO, and it is made to return and is set to N2.

[0057] That is, HC in inflow exhaust gas and CO react immediately with oxygen O2- on Platinum Pt, or O2- first, and are made to oxidize, and if HC and CO still remain even if oxygen O2- or O2- on Platinum Pt is subsequently consumed, NOx emitted from the NOx catalyst 17 and NOx in inflow exhaust gas will be made to return them to N2 by this HC and CO.

[0058] Thus, when NO2 or NO stops existing on the front face of Platinum Pt, NO2 or NO is emitted to a degree from a degree from the NOx catalyst 17, and it is made to return to N2 further. Therefore, when an exhaust air air-fuel ratio is made into theoretical air fuel ratio or Ricci, NOx will be emitted to the inside of a short time from the NOx catalyst 17.

[0059] Thus, if an exhaust air air-fuel ratio becomes Lean, NOx will be absorbed by the NOx catalyst 17, and if an exhaust air air-fuel ratio is made into theoretical air fuel ratio or Ricci, NOx will be emitted to the inside of a short time from the NOx catalyst 17, and will be returned to N2. Therefore, blowdown of NOx to

the inside of atmospheric air can be prevented.

[0060] By the way, since gaseous mixture supplied in a combustion chamber 3 is made into Ricci at the time of full load running, and gaseous mixture is made into theoretical air fuel ratio at the time of heavy load operation and gaseous mixture is made into Lean at the time of load operation in low as mentioned above with the gestalt of this operation NOx in exhaust gas will be absorbed by the NOx catalyst 17 at the time of load operation in low, and NOx will be emitted and returned from the NOx catalyst 17 at the time of full load running and heavy load operation etc. Frequency, such as full load running or heavy load operation, is low, and if there is much frequency of load operation in low and the operation time excels, bleedoff and reduction of NOx stop meeting the deadline, the absorptance of NOx of the NOx catalyst 17 will be saturated, and it will become impossible however, to absorb NOx.

[0061] then -- the gestalt of this operation -- Lean -- the time of performing inside low load driving, when combustion of gaseous mixture is performed -- comparatively -- alike -- a short period -- a spike ---like (short time) -- SUTOIKI or Ricci -- the air-fuel ratio of gaseous mixture is controlled so that combustion of gaseous mixture is performed, and bleedoff and reduction of NOx are performed in short period. Thus, for the absorption/emission of NOx, it has called it the Lean Ricci Spike control to control "Lean", and the "spike-theoretical air fuel ratio or the Ricci air-fuel ratio (Ricci Spike)" to be repeated by turns the period with an exhaust air air-fuel ratio (the gestalt of this operation air-fuel ratio of gaseous mixture) short in comparison. In addition, in this application, the Lean Ricci Spike control shall be included in Lean Air Fuel Ratio Control.

[0062] On the other hand, if sulfur (S) is contained in the fuel and the sulfur in a fuel burns, sulfur oxides (SOx), such as SO2 and SO3, will be generated, and these SOx in exhaust gas will also absorb the NOx catalyst 17. It is thought that the SOx absorption mechanism of the NOx catalyst 17 is the same as a NOx absorption mechanism. Namely, if it explains taking the case of the case where Platinum Pt and Barium Ba are made to ****, on support like the time of explaining the absorption mechanism of NOx, as mentioned above When an exhaust air air-fuel ratio is Lean, oxygen O2 has adhered to the front face of the platinum Pt of the NOx catalyst 17 in the form of O2- or O2-, and SOx in inflow exhaust gas (for example, SO2) oxidizes on the front face of Platinum Pt, and serves as SO3.

[0063] Then, generated SO3 is absorbed in Ba, combines with the barium oxide BaO, oxidizing further on the front face of Platinum Pt, is diffused in Ba in the form of sulfate ion SO42-, and forms a sulfate BaSO4. Since it is easy to make a crystal big and rough and it tends [comparatively] to be stabilized, once it is generated, the decomposition and bleedoff of this BaSO4 will be hard to be done. And if the amount of generation of BaSO4 in the NOx catalyst 17 increases, the amount of BaO which can participate in absorption of the NOx catalyst 17 will decrease, and the absorptance of NOx will decline. It is this, i.e., SOx poisoning. Therefore, in order to maintain the NOx absorptance of the NOx catalyst 17 highly, it is necessary to perform SOx poisoning recovery for making SOx absorbed by the NOx catalyst 17 to proper timing emit.

[0064] In order to make SOx emit from the NOx catalyst 17, it turns out that it is necessary to make the air-fuel ratio of the flowing exhaust gas into theoretical air fuel ratio or the Ricci air-fuel ratio and, and it is easy to emit, so that whenever [catalyst temperature / of the NOx catalyst 17] is high. Then, SOx poisoning recovery makes whenever [catalyst temperature / of the NOx catalyst 17] the predetermined elevated temperature (this is hereafter called SOx bleedoff temperature) which is easy to be emitted to SOx, and performs it by passing the exhaust gas of theoretical air fuel ratio or the Ricci air-fuel ratio for the NOx catalyst 17.

[0065] And with the gestalt of this operation, also when making the air-fuel ratio of exhaust gas into theoretical air fuel ratio or the Ricci air-fuel ratio for SOx poisoning recovery, it carries out by controlling the air-fuel ratio of the gaseous mixture which controls the fuel quantity injected from a fuel injection valve 11 by ECU30, and is supplied to a combustion chamber 3 to theoretical air fuel ratio or the Ricci air-fuel ratio. Therefore, ECU30 and a fuel injection valve 11 constitute a part of poisoning recovery means.

[0066] Next, the heat deterioration degree detection approach of the NOx catalyst 17 of the exhaust emission control device in the gestalt of this operation is explained. Drawing 5 performs SOx poisoning recovery until SOx by which occlusion was carried out to the NOx catalyst 17 whenever SOx poisoning of the NOx catalyst 17 reached predetermined level is emitted thoroughly, and it makes a graph one experimental result which measured the NOx clarification engine performance of the NOx catalyst 17 immediately after the SOx poisoning recovery. Whenever the NOx clarification engine performance of the NOx catalyst 17 performs SOx poisoning recovery, it is falling.

[0067] As mentioned above, SOx poisoning degradation of the NOx catalyst 17 is recoverable by

performing SOx poisoning recovery, but since poisoning recovery is impossible about the heat deterioration of the NOx catalyst 17, the engine-performance recovery part immediately after SOx poisoning recovery can be called degradation resulting from SOx poisoning, and an engine-performance recovery impossible part can be called degradation resulting from heat deterioration.

[0068] Therefore, if the NOx occlusion capacity at the time of the new article of the NOx catalyst 17 and the NOx occlusion capacity of the NOx catalyst 17 immediately after SOx poisoning recovery are detectable, the degree of heat deterioration is detectable from the difference of such NOx occlusion capacity.

[0069] With the gestalt of this operation, NOx occlusion capacity is detected as follows. First, passing the exhaust gas of the Lean air-fuel ratio is continued for the NOx catalyst 17, the NOx occlusion capacity of the NOx catalyst 17 is saturated, and it changes into the condition that the occlusion of the NOx cannot be carried out any more. Next, the air-fuel ratio of the exhaust gas which flows into the NOx catalyst 17, i.e., close gas, is changed from Lean to Ricci, passing the exhaust gas of the Ricci air-fuel ratio is continued for the NOx catalyst 17, and the whole quantity of NOx by which occlusion was carried out to the NOx catalyst 17 is made to emit and return. Even if it changes the air-fuel ratio of close gas from Lean to Ricci at this time, the air-fuel ratio of the exhaust gas of the outlet of the NOx catalyst 17, i.e., appearance gas, does not immediately change to Ricci, but it becomes near the theoretical air fuel ratio for a while. This is because HC and CO in close gas are consumed as a reducing agent by the reduction of NOx by which occlusion was carried out to the NOx catalyst 17. And when all the NOx by which occlusion was carried out to the NOx catalyst 17 is emitted and returned and HC and CO in close gas are no longer consumed as a reducing agent, the air-fuel ratio of appearance gas changes to Ricci.

[0070] After saturating the NOx occlusion capacity of the NOx catalyst 17 in this way, therefore, bleedoff / reduction processing of NOx Perform (this processing is hereafter called saturation NOx bleedoff processing), and the air-fuel ratio sensor 27 detects the air-fuel ratio of the appearance gas at that time. If time amount until it comes out after starting saturation NOx bleedoff processing, it will come out if it puts in another way time for the air-fuel ratio of gas to hold theoretical air fuel ratio, and the air-fuel ratio of gas changes from theoretical air fuel ratio to Ricci is measured That duration (this duration is hereafter called Ricci change rate time amount) becomes a barometer showing the NOx occlusion capacity of the NOx catalyst 17, namely, becomes the barometer of the clarification engine performance of the NOx catalyst 17.

[0071] Drawing 6 comes out with the air-fuel ratio of the close gas at the time of saturation NOx bleedoff processing, an example of the temporal response of the air-fuel ratio of gas is shown, and the Ricci change rate time amount of the NOx catalyst 17 for which heat deterioration advanced to some extent is set to t_2 [shorter than t_1] to the Ricci change rate time amount being t_1 with the new NOx catalyst 17.

[0072] Moreover, with the gestalt of this operation, the Ricci change rate time amount is used and judged also to the judgment of a stage which performs SOx poisoning recovery to the NOx catalyst 17. If it explains in full detail, in the exhaust emission control device of the gestalt of this operation, saturation NOx bleedoff processing will be performed, for example to the NOx catalyst 17 to the proper timing for every fixed mileage and every fixed fuel consumption, and the Ricci change rate time amount at that time will be measured. And since the NOx clarification engine performance of the NOx catalyst 17 can regard it as that which fell to predetermined level when the measured Ricci change rate time amount becomes shorter than the predetermined time t_3 shown in drawing 6 , it judges that this time is the stage when SOx poisoning recovery should be performed.

[0073] furthermore, in the exhaust emission control device of the gestalt of this operation After completion of SOx poisoning recovery, perform saturation NOx bleedoff processing and the Ricci change rate time amount is measured. When the difference of the measured Ricci change rate time amount t_2 and the Ricci change rate time amount t_1 of the new NOx catalyst 17 is computed and the difference becomes longer than predetermined time t_4 It judges that the heat deterioration of the NOx catalyst 17 progressed to the predetermined degree, and a heat deterioration control means is operated that heat deterioration should be controlled. in addition, the Ricci change rate time amount t_1 of the new NOx catalyst 17 is found experimentally beforehand, and is memorized to ROM32 of ECU30, and a heat deterioration control means should be operated -- ** -- the threshold t_4 when judging is also set up beforehand, and is memorized to ROM of ECU30.

[0074] Next, if the control approach of heat deterioration is explained, when it becomes slowdown operation, generally the fuel cut will be performed with the engine, for example, but when heat deterioration advances to a predetermined degree, an engine is in an elevated-temperature operation region and it becomes slowdown operation, heat deterioration can be controlled by forbidding a fuel cut. If this has an engine in an elevated-temperature operation region, the NOx catalyst 17 will also be in the elevated-

temperature condition, and when a fuel cut is performed at this time, exhaust gas with a high oxygen density will flow into the NOx catalyst 17. When whenever [catalyst temperature] is the same as for sintering of the catalyst matter (Pt) in the NOx catalyst 17, it is known that the speed of advance of sintering is so quick that an oxygen density is high. Therefore, if a fuel cut is performed at the time of the slowdown of an elevated-temperature operation region, when whenever [catalyst temperature] is an elevated temperature, the high exhaust gas of an oxygen density will flow and sintering will be promoted. Then, if a fuel cut is forbidden when it is in an elevated-temperature operation region and becomes slowdown operation, sintering of the NOx catalyst 17 can be controlled and heat deterioration can be controlled. In this case, the fuel cut prohibition control which forbids a fuel cut in an elevated-temperature operation region constitutes a heat deterioration control means.

[0075] Moreover, as the control approach of another heat deterioration, when heat deterioration advances to a predetermined degree, there is a method of making a Lean operating range in an engine elevated-temperature operation region decrease from it or before (namely, while heat deterioration is not advancing to said predetermined degree). This is also the same reason as the above-mentioned, and is because the direction which made the oxygen density of close gas low can control the heat deterioration of the NOx catalyst 17 when whenever [catalyst temperature / of the NOx catalyst 17] is high. As the concrete control approach, before heat deterioration advances to a predetermined degree, some or all of a field that was elevated-temperature operation regions and was the Lean operating range is henceforth changed into a SUTOIKI (theoretical air fuel ratio) operating range, when heat deterioration advances to a predetermined degree. In this case, the Lean operating-range reduction control which decreases a Lean operating range in an elevated-temperature operation region constitutes a heat deterioration control means.

[0076] Next, with reference to drawing 7, the heat deterioration judging manipulation routine of the NOx catalyst 17 in the gestalt of this operation is explained. The flow chart which consists of each step which constitutes this control routine is memorized by ROM32 of ECU30, and this control routine is performed by CPU34 for every fixed time amount.

[0077] <Step 101> ECU100 judges first whether it is the stage when SOx poisoning recovery should be performed to the NOx catalyst 17 in step 101. As mentioned above, with the gestalt of this operation, the judgment of being a SOx poisoning recovery activation stage performs saturation NOx bleedoff processing for every predetermined period, and it judges that the time of the Ricci change rate time amount then measured becoming smaller than a threshold t3 is the stage when SOx poisoning recovery should be performed. When a negative judging is carried out at step 101, ECU30 once ends activation of this routine.

[0078] When an affirmation judging is carried out at <step 102> step 101, ECU30 progresses to step 102 and performs SOx poisoning recovery. SOx poisoning recovery is performed by performing predetermined temperature-up processing, and carrying out whenever [catalyst temperature / of the NOx catalyst 17] beyond SOx bleedoff temperature, and making the air-fuel ratio of the close gas of the NOx catalyst 17 into Ricci a little than SUTOIKI, when the NOx catalyst 17 has not reached SOx bleedoff temperature.

[0079] <Step 103>, next ECU30 progress to step 103, and judge whether SOx poisoning recovery was completed. Here, SOx poisoning recovery is performed until it emits nearly thoroughly SOx absorbed by the NOx catalyst 17. About the judgment of completion of SOx poisoning recovery, it mentions later. When a negative judging is carried out at step 103, ECU30 continues activation of return and SOx poisoning recovery to step 102.

[0080] When an affirmation judging is carried out at <step 104,105> step 103, ECU30 progresses to step 104, performs saturation NOx bleedoff processing, further, progresses to step 105 and measures the Ricci change rate time amount t.

[0081] <Step 106>, next ECU30 progress to step 106, and compute the difference of the Ricci change rate time amount t1 of the new NOx catalyst 17 beforehand memorized by ROM32 of ECU30, and the Ricci change rate time amount t measured at step 105. That is, the heat deterioration degree of the NOx catalyst 17 at present is computed.

[0082] <Step 107>, next ECU30 progress to step 107, and more than 4 [threshold t] the difference (heat deterioration degree) of the Ricci change rate time amount computed at step 106 set up beforehand, they judge *****. When a negative judging is carried out at step 107, ECU30 once ends activation of this routine.

[0083] When an affirmation judging is carried out at <step 108> step 107, it judges with the heat deterioration degree of the NOx catalyst 17 having reached to predetermined level, and ECU30 progresses to step 108, operates a heat deterioration control means, and once ends activation of this routine. Progress of the heat deterioration of the future NOx catalysts 17 is controlled by actuation of a heat deterioration control

means, i.e., activation of the fuel cut prohibition control in the elevated-temperature operation region mentioned above or activation of the Lean operating-range reduction control in an elevated-temperature operation region.

[0084] In addition, in the gestalt of this operation, when ECU30 performs step 101 among heat deterioration judging manipulation routines, the poisoning recovery activation stage judging means in this invention is realized. Moreover, when ECU30 performs step 102, the poisoning recovery means in this invention is realized. Moreover, when ECU30 performs step 104 and step 105, the occlusion capacity detection means in this invention is realized and ECU30 performs step 106 and step 107, the heat deterioration judging means in this invention is realized.

[0085] Next, the SOx poisoning recovery in the gestalt of this operation is explained with reference to drawing 8. Drawing 8 is the air-fuel ratio of the close gas of the NOx catalyst 17 at the time of the SOx poisoning recovery in the gestalt of this operation, the SOx concentration of the close gas detected by the close gas SOx sensor 23, and drawing that was detected by the appearance gas SOx sensor 24 and in which having come out and having shown aging of the SOx concentration of gas. In addition, whenever [catalyst temperature / of the NOx catalyst 17] shall have become during a SOx poisoning recovery activation period beyond SOx bleedoff temperature.

[0086] First, the air-fuel ratio of close gas is changed into theoretical air fuel ratio from the Lean air-fuel ratio by SOx poisoning recovery activation command, and the gradual increase of whenever [Ricci / of the air-fuel ratio of close gas] is carried out further. And when in agreement with the close gas SOx concentration which was detected by the appearance gas SOx sensor 24 and by which it came out and gas SOx concentration was detected by the close gas SOx sensor 23, the air-fuel ratio of close gas is uniformly held with the Ricci air-fuel ratio when being in agreement. Since SOx is substantially emitted from the NOx catalyst 17 after appearance gas SOx concentration is in agreement with close gas SOx concentration, the direction of appearance gas SOx concentration becomes larger than close gas SOx concentration, and comes out by predetermined concentration, and gas SOx concentration becomes almost fixed. If bleedoff of SOx from the NOx catalyst 17 furthermore continues after that, in order that the SOx burst size from the NOx catalyst 17 may decrease, appearance gas SOx concentration falls, and if SOx which remains for the NOx catalyst 17 is lost, appearance gas SOx concentration becomes lower than close gas SOx concentration. Therefore, if appearance gas SOx concentration continues SOx poisoning recovery until only a predetermined value becomes low rather than close gas SOx concentration, it can be considered that the NOx catalyst 17 was recovered nearly thoroughly from SOx poisoning. With the gestalt of this operation, it decided to continue SOx poisoning recovery until appearance gas SOx concentration became below the completion level of poisoning recovery in drawing 8.

[0087] [the gestalt of the 2nd operation] -- the gestalt of this operation explains the case where the heat deterioration degree of the NOx catalyst 17 of an exhaust emission control device is detected based on change of the rate of NOx clarification of a NOx catalyst. Drawing 13 is the schematic diagram of the exhaust emission control device in the gestalt of this operation, four cylinders 41 are formed in the engine body 40, and the fuel injection valve 42 is attached in the inlet port connected to each cylinder 41. The inlet manifold 43 is connected with the air cleaner 45 through the air intake duct 44. Moreover, the throttle valve 46 is formed in the air intake duct 44.

[0088] On the other hand, it connects with the casing 49 which built in the occlusion reduction type NOx catalyst 50 through an exhaust manifold 47 and an exhaust pipe 48, and casing 49 is connected to the muffler which is not illustrated through an exhaust pipe 51. About the configuration of other ECUs30 and NOx catalyst 17 grade, since it is the same as that of the exhaust emission control device in the gestalt of the 1st operation, the same sign is attached and explanation is omitted.

[0089] The appearance gas NOx sensor 50 which generates the output voltage proportional to the NOx concentration of the appearance gas which flows out of the NOx catalyst 17 is formed in the lower stream of a river of casing 49, and this output voltage is inputted into the input port 35 of ECU30. Drawing 14 is drawing showing an example of the rate of NOx clarification by the NOx catalyst 17. Close [NOx] shows the NOx concentration per unit time amount in the exhaust gas which flows into the NOx catalyst 17, and Appearance NOx shows the NOx concentration per unit time amount in the exhaust gas which flows out of the NOx catalyst 17 here. Here, if the NOx concentration per unit time amount in the exhaust gas discharged from the NOx catalyst 17 reaches a threshold X, NOx by which makes exhaust gas SUTOIKI or Ricci and occlusion is carried out to the NOx catalyst 17 will be made to emit and return, and the NOx occlusion capacity of the NOx catalyst 17 will be recovered. However, if operation in Lean's condition continues [exhaust gas] and occlusion of the NOx in exhaust gas is carried out to the NOx catalyst 17, a saturation

state will be reached again and the concentration of Appearance NOx will reach ***** X. Then, by performing Ricci Spike again, NOx is emitted and it returns.

[0090] However, since SOx poisoning of the NOx catalyst 17 will reach predetermined level as explained in full detail in the gestalt of the 1st operation if this is repeated, SOx poisoning recovery will be performed. And although SOx poisoning of the NOx catalyst 17 is recoverable by performing SOx poisoning recovery, since the heat deterioration of the NOx catalyst 17 is unrecoverable, it can be supposed that it is the engine-performance recovery impossible part immediately after SOx poisoning recovery the degradation resulting from heat deterioration.

[0091] Therefore, the rate of NOx clarification at the time of the new article of the NOx catalyst 17 and the rate of NOx clarification immediately after the SOx poisoning recovery are measured, and if this is compared, the degree of heat deterioration can be known from the difference of the NOx clarification engine performance. With the rate of NOx clarification, it asks here based on the amount of NOx in the exhaust gas which flows into a NOx catalyst (the amount of close NOx), and the amount of NOx in the exhaust gas by the NOx detection means installed in the lower stream of a river of a NOx catalyst (the amount of appearance NOx). At this time, an amount close [said / NOx] is computable by attaching a NOx sensor in the flueway of the upstream of the NOx catalyst 17 from the NOx concentration per unit time amount from that output value, and the integrated value of the amount of exhaust gas. Moreover, an amount close [NOx] is calculated also by the following approaches.

[0092] namely, Lean -- the amount of NOx discharged by the engine per unit time amount increases, so that the amount of NOx discharged by the engine per unit time amount increases, so that an engine load becomes high, when gaseous mixture has burned, and an engine rotational frequency becomes high. Therefore, the amount of NOx per unit time amount serves as an engine load and a function of an engine rotational frequency. In this case, since an engine load can be represented with the absolute pressure in a surge tank, the amount NOXA of the appearance NOx per unit time amount serves as the absolute pressure PM in a surge tank, and a function of the engine rotational frequency N. Therefore, in the gestalt of this operation, the amount of NOx per unit time amount is beforehand calculated by experiment as a function of absolute pressure PM and the engine rotational frequency N, and it memorizes in RAM of ECU30 in the form of a map where this is shown in drawing 16.

[0093] On the other hand, by attaching a NOx sensor in the flueway of the lower stream of a river of the NOx catalyst 17, since the NOx concentration per unit time amount is detected from that output value, the amount of Appearance NOx is computable based on the integrated value of this NOx concentration and the amount of exhaust gas. Thus, the rate of NOx clarification of the NOx catalyst 17 can be measured, and the stage of SOx poisoning playback can be judged by comparing this with the early rate of clarification in new, or the rate of need clarification.

[0094] Moreover, if the rate of NOx clarification at the time of the new article of the NOx catalyst 17 and the rate of NOx clarification of the NOx catalyst 17 immediately after SOx poisoning recovery can be detected and these can be compared, the degree of the heat deterioration of the NOx catalyst 17 is detectable from the difference of those rates of clarification. in addition, it asks for the new rate of NOx clarification and the new rate of need clarification of the NOx catalyst 17 experimentally beforehand, and they are memorized to ROM32 of ECU30, and a heat deterioration control means should be operated -- ** -- the rate of need clarification when judging is also set up beforehand, and is memorized to ROM of ECU30.

[0095] With the gestalt of this operation, the NOx clarification engine performance is detected as follows. First, passing the exhaust gas of the Lean air-fuel ratio is continued for the NOx catalyst 17, the NOx occlusion capacity of the NOx catalyst 17 is saturated, and it changes into the condition that the occlusion of the NOx cannot be carried out any more. At this time, the clarification engine performance of a NOx catalyst is measured in consideration of a temperature window.

[0096] Next, the air-fuel ratio of the exhaust gas which flows into the NOx catalyst 17, i.e., close gas, is changed from Lean to Ricci, passing the exhaust gas of the Ricci air-fuel ratio is continued for the NOx catalyst 17, and the whole quantity of NOx by which occlusion was carried out to the NOx catalyst 17 is made to emit and return. Even if it changes the air-fuel ratio of close gas from Lean to Ricci at this time, the air-fuel ratio of the exhaust gas of the outlet of the NOx catalyst 17, i.e., appearance gas, does not immediately change to Ricci, but it becomes near the theoretical air fuel ratio for a while. This is because HC and CO in close gas are consumed as a reducing agent by the reduction of NOx by which occlusion was carried out to the NOx catalyst 17. And when all the NOx by which occlusion was carried out is emitted and returned to the NOx catalyst 17 and HC and CO in close gas are no longer consumed as a reducing agent, the air-fuel ratio of appearance gas changes to Ricci.

[0097] Moreover, with the gestalt of this operation, it judges by whether the rate of NOx clarification became below a predetermined value for the judgment of a stage which performs SOx poisoning recovery to the NOx catalyst 17. If it explains in full detail, in the exhaust emission control device of the gestalt of this operation, saturation NOx bleedoff processing will be performed, for example to the NOx catalyst 17 to the proper timing for every fixed mileage and every fixed fuel consumption, and the rate of NOx clarification at that time will be measured. By the appearance side NOx sensor 50, this measurement grasps the clarification engine performance of the NOx catalyst in each load and temperature conditions.

[0098] And when the measured rate of NOx clarification falls rather than the threshold \times shown in drawing 14, the NOx clarification engine performance of the NOx catalyst 17 regards it as that which fell to predetermined level. Moreover, it judges that this time is the stage when SOx poisoning recovery should be performed.

[0099] If SOx poisoning recovery is completed, the rate of NOx clarification will be measured, and it judges whether the engine performance of a NOx catalyst was recovered. As shown in drawing 15, the rate of NOx clarification judges this by whether it exceeded the rate of need clarification in the range of predetermined temperature (for example, 300 degrees C - about 420 degrees C). In drawing 1515, a NOx catalyst shows the rate of NOx clarification at the time of being ** at the new article time, and ** shows the rate of NOx clarification at the time of SOx poisoning. ** In the condition, SOx poisoning recovery is in a required condition, and ** shows the rate of clarification after SOx poisoning recovery.

[0100] When the rate of need clarification is not secured next, Ricci Spike according to the degree of the heat deterioration of a NOx catalyst is performed. this -- an internal combustion engine -- setting -- Lean -- the time of performing inside low load driving, when combustion of gaseous mixture is performed -- comparatively -- alike -- a short period -- a spike ---like (short time) -- SUTOIKI or Ricci -- if recovery of degradation is inadequate, Ricci Spike will be made to increase, although the air-fuel ratio of gaseous mixture is controlled so that combustion of gaseous mixture is performed, and bleedoff and reduction of NOx are performed in short period This has both shortenings of buildup of Ricci Spike's amount or buildup of Ricci Spike's count, i.e., Ricci Spike's period, and as it is proportional to the degree of heat deterioration, it performs either or both.

[0101] Next, in the exhaust emission control device of the gestalt of this operation, after carrying out said Ricci Spike control, the rate of NOx clarification is measured, it judges that the heat deterioration of the NOx catalyst 17 progressed to extent in which engine-performance recovery is impossible when that rate of clarification was below predetermined level, and a heat deterioration control means is operated that heat deterioration should be controlled. That is, it is the case where sufficient rate of NOx clarification is not securable even if it carries out such control.

[0102] First, Lean operation in a temperature field deficient in performance is forbidden. Rather than the time of heat deterioration not advancing to a predetermined degree, this decreases a Lean operating range and controls the heat deterioration of the NOx catalyst 17 by making low the close gas oxygen density of the NOx catalyst 17. As specifically shown in drawing 15, in the temperature field (field which does not return even if it recovers) to which the engine performance of a NOx catalyst becomes below a rate of need clarification, Lean operation is forbidden and this field is changed into a SUTOIKI operating range.

[0103] Next, as explained in the gestalt of the 1st operation as the control approach of heat deterioration different from this, or the control approach of the heat deterioration which combines with the above and is performed, even when an engine is in an elevated-temperature operation region and it becomes slowdown operation, heat deterioration is controlled by forbidding a fuel cut. Moreover, as the control approach of heat deterioration, the approach of decreasing a Lean operating range in an engine elevated-temperature operation region is adopted rather than the time of heat deterioration not advancing to a predetermined degree. Although this overlaps the range of prohibition of Lean operation in the temperature field deficient in performance mentioned above, in an elevated-temperature operating range beyond predetermined temperature, Lean operation is forbidden altogether.

[0104] Hereafter, with reference to drawing 17, the heat deterioration judging manipulation routine of the NOx catalyst 17 in the gestalt of this operation is explained. The flow chart which consists of each step which constitutes this control routine is memorized by ROM32 of ECU30, and this control routine is performed by CPU34 for every fixed time amount.

[0105] <Step 201> ECU100 judges first whether it is the stage when SOx poisoning recovery should be performed to the NOx catalyst 17 in step 201. The judgment of being a SOx poisoning recovery activation stage performs saturation NOx bleedoff processing for every predetermined period, and the rate of NOx clarification is measured after completion of bleedoff processing. This is computed based on the output

value of the NOx sensor 50 by the side of appearance. It judges that the time of this value becoming lower than the rate of need clarification is the stage when SOx poisoning recovery should be performed. When a negative judging is carried out at step 201, ECU30 once ends activation of this routine.

[0106] When an affirmation judging is carried out at <step 202> step 201, ECU30 progresses to step 202 and performs SOx poisoning recovery. SOx poisoning recovery is performed by performing predetermined temperature-up processing, and carrying out whenever [catalyst temperature / of the NOx catalyst 17] beyond SOx bleedoff temperature, and making the air-fuel ratio of the close gas of the NOx catalyst 17 into Ricci a little than SUTOIKI, when the NOx catalyst 17 has not reached SOx bleedoff temperature.

[0107] <Step 203>, next ECU30 progress to step 203, and judge whether SOx poisoning recovery was completed. Here, SOx poisoning recovery is performed until it emits nearly thoroughly SOx absorbed by the NOx catalyst 17. When a negative judging is carried out at step 203, ECU30 continues activation of return and SOx poisoning recovery to step 202.

[0108] When an affirmation judging is carried out at <step 204> step 203, ECU30 progresses to step 204, performs saturation NOx bleedoff processing, further, progresses to step 205 and measures the rate of NOx clarification.

[0109] <Step 205>, next ECU30 progress to step 205, and measure the rate of NOx clarification of the NOx catalyst 17.

[0110] It progresses to <step 206> step 206, ECU30 becomes more than the rate of need clarification that the rate of NOx clarification measured at step 206 set up beforehand, and it judges whether the NOx catalyst function was recovered. When an affirmation judging is carried out at step 206, ECU30 once ends activation of this routine.

[0111] When a negative judging is carried out at <step 207> step 206, the Ricci Spike control is performed and the engine performance of the NOx catalyst 17 is tried.

[0112] By the Ricci Spike control performed at <step 208> step 207, it judges whether the rate of NOx clarification of a NOx catalyst was recovered. This is judged by whether the rate of NOx clarification in a predetermined temperature requirement is lower than the rate of need clarification. If the rate of clarification is more than a rate of need clarification, ECU30 will once end activation of this routine.

[0113] If the rate of NOx clarification is below a rate of need clarification in <step 209> step 208, Lean operation in the temperature field which runs short of the engine performance will be forbidden. When the rate of NOx clarification comes out below the rate of need clarification, engine-performance recovery is made impossible and heat deterioration is judged to be a large thing.

[0114] <Step 210> Heat deterioration inhibitory control of further others is carried out. This is control against reduction of a Lean operating range in an elevated-temperature operating range, and a fail cut in an elevated-temperature operation region. Thereby, progress of the heat deterioration of the future NOx catalysts 17 is controlled.

[0115] In addition, in the gestalt of this operation, when ECU30 performs step 201 among heat deterioration judging manipulation routines, the poisoning recovery activation stage judging means in the 2nd invention is realized, and ECU30 performs step 202, a poisoning recovery means is realized and ECU30 performs step 204 and step 205, the rate measurement means of NOx clarification is realized.

[0116] Moreover, when the rate of NOx clarification is not secured by the Ricci Spike control in the gestalt of this operation, it judges that the heat deterioration of the NOx catalyst 17 is large, and exchange of a catalyst can be urged.

[0117] Gestalt] of operation of others [[] The judgment of the completion of SOx poisoning recovery activation can be judged by whether the SOx poisoning recovery execution time exceeded the predetermined time set up beforehand. In this case, poisoning recovery time amount required in order to emit nearly thoroughly SOx by which occlusion was carried out to the NOx catalyst 17 is found experimentally beforehand, and ROM32 of ECU30 is made to memorize this.

[0118] The judgment of being a SOx poisoning recovery activation stage may judge with the time of the amount of sulfur which passes the NOx catalyst 17 exceeding the specified quantity (henceforth the amount of allowance sulfur) being a SOx poisoning recovery activation stage.

[0119] In that case, the sulfur concentration in a fuel is presumed from the SOx concentration of the close gas detected by the close gas SOx sensor 23, and based on the presumed sulfur concentration in this fuel, the fuel consumption or mileage corresponding to said amount of allowance sulfur can be computed, and it can judge that the time of reaching that fuel consumption or mileage is a SOx poisoning recovery activation stage. Furthermore, the presumed sulfur concentration in a fuel is displayed on the panel in front of a driver's seat etc., and the frequency of SOx poisoning recovery may enable it to distinguish about in this

case.

[0120] Or based on the inhalation air content of the SOx concentration of close gas, and an engine detected by the close gas SOx sensor 23, the amount of SOx which flows into the NOx catalyst 17 can be computed, and it can judge that the time of the integrated value exceeding the specified quantity is a SOx poisoning recovery activation stage.

[0121] Thus, when judging that the time of the amount of sulfur which passes the NOx catalyst 17 exceeding the amount of allowance sulfur is a SOx poisoning recovery activation stage and judging the completion of SOx poisoning recovery activation in the SOx poisoning recovery execution time like the above-mentioned, the appearance gas SOx sensor 24 can be omitted.

[0122] Moreover, the judgment of being a SOx poisoning recovery activation stage may presume the amount of SOx by which occlusion was carried out to the NOx catalyst 17, and may judge with the time of this amount of presumed occlusion SOx exceeding the specified quantity being a SOx poisoning recovery activation stage. in addition, as shown in drawing 9 , presumption of the amount of occlusion SOx came out with the SOx concentration of the close gas detected by the close gas SOx sensor 23, and was detected by the gas SOx sensor 24 -- coming out -- the concentration of the SOx concentration of gas -- difference can compute as that by which occlusion is carried out to the NOx catalyst 17 based on the inhalation air content of this SOx concentration difference (close gas SOx concentration-appearance gas SOx concentration) and an engine. And it can do in this way, a SOx deposition counter can integrate the amount of occlusion SOx which carried out calculation presumption, and it can judge that the time of the counted value of a SOx deposition counter exceeding a predetermined value is a SOx poisoning recovery activation stage.

[0123] Moreover, when it has a SOx deposition counter in this way, the judgment of completion of SOx poisoning recovery can also be performed as follows. Are during a SOx poisoning recovery activation period, and come out and it sets at the period when gas SOx concentration is larger than close gas SOx concentration. the concentration of appearance gas SOx concentration and close gas SOx concentration, since difference can presume that it is SOx emitted from the NOx catalyst 17 The amount of SOx emitted from the NOx catalyst 17 based on the inhalation air content of this SOx concentration difference (appearance gas SOx concentration-close gas SOx concentration) and an engine is computed. As the SOx burst size which carried out calculation presumption is subtracted with said SOx deposition counter and it is shown in drawing 10 , when the counted value of a SOx deposition counter falls to a predetermined value (the completion level of poisoning recovery) Activation of SOx poisoning recovery can be ended as what SOx poisoning recovery completed.

[0124] Furthermore, the judgment of being a SOx poisoning recovery activation stage may judge that the time of the SOx concentration of appearance gas approaching the SOx concentration of close gas to predetermined level is a SOx poisoning recovery activation stage. As shown in drawing 11 , the SOx concentration of the appearance gas of the NOx catalyst 17 approaches the SOx concentration of close gas as SOx poisoning advances. Therefore, it can be said that extent of access to the SOx concentration of the close gas of the SOx concentration of appearance gas supports the degree of SOx poisoning. Then, when the SOx concentration of appearance gas approaches the SOx concentration of close gas to what extent beforehand, it sets up whether SOx poisoning recovery is performed, and it can judge that the time of being detected by the appearance gas SOx sensor 24 when it came out and the SOx concentration of gas exceeded said set-up SOx concentration is a SOx poisoning recovery activation stage.

[0125] Although the SOx concentration of the exhaust gas which forms the close gas SOx sensor 23 in the upstream of the NOx catalyst 17, and flows into the NOx catalyst 17 by this close gas SOx sensor 23 is detected with the gestalt of each above-mentioned operation Since it is dependent on the sulfur concentration, the fuel quantity, and the amount of exhaust gas in a fuel, the SOx concentration of the exhaust gas which flows into the NOx catalyst 17 can be presumed from engine operation conditions (fuel oil consumption, an air-fuel ratio, an inhalation air content, engine speed, etc.), when the sulfur concentration in a fuel is known. Therefore, instead of forming the close gas SOx sensor 23, the SOx concentration of catalyst close gas is computed by ECU30, and you may make it presume from an engine operation condition in that case.

[0126] Although the example applied to the gasoline engine explained this invention with the gestalt of operation mentioned above, of course, this invention is applicable to a diesel power plant. Since it is carried out in the Lean region farther [combustion in a combustion chamber] than SUTOIKI in the case of a diesel power plant, the air-fuel ratio of the exhaust gas which flows into the NOx catalyst 17 in the usual engine operational status is very Lean, and although absorption of NOx and SOx is performed, bleedoff of NOx and SOx is hardly performed.

[0127] Moreover, an exhaust air air-fuel ratio is made into SUTOIKI or Ricci by making into SUTOIKI or Ricci gaseous mixture supplied to a combustion chamber 3 as mentioned above in the case of the gasoline engine. Although NO_x and SO_x which the oxygen density in exhaust gas is reduced and are absorbed by the NO_x catalyst 17 can be made to emit In the case of a diesel power plant, if gaseous mixture supplied to a combustion chamber is made into SUTOIKI or Ricci, in the case of combustion, there can be the problem of soot being generated and cannot adopt.

[0128] Therefore, in order to make an exhaust air air-fuel ratio into SUTOIKI or Ricci, and to obtain an engine output, it is necessary when applying this invention to a diesel power plant, to supply a reducing agent (for example, gas oil which is a fuel) into exhaust gas apart from burning a fuel. Also by subinjecting a fuel in a cylinder in an intake stroke, an expansion stroke, or an exhaust stroke, supply of the reducing agent to exhaust gas is possible, or possible also by supplying a reducing agent in the flueway of the upstream of the NO_x catalyst 17.

[0129] In addition, even if it is a diesel power plant, when it has exhaust-gas-recirculation equipment (the so-called EGR equipment), it is possible by introducing exhaust-gas-recirculation gas into a combustion chamber so much to make the air-fuel ratio of exhaust gas into theoretical air fuel ratio or the Ricci air-fuel ratio.

[0130]

[Effect of the Invention] According to the exhaust emission control device of the internal combustion engine concerning this invention, the heat deterioration degree of an occlusion reduction type NO_x catalyst can be judged by having a heat deterioration judging means to judge the heat deterioration degree of an occlusion reduction type NO_x catalyst. Therefore, it can know that it is what the NO_x clarification engine performance falls and cannot recover this, and the situation that NO_x in exhaust gas is no longer purified by exchange of a catalyst etc. can be avoided.

[0131] Moreover, the exhaust emission control device of the internal combustion engine concerning this invention It has a heat deterioration control means to control the heat deterioration of said occlusion reduction type NO_x catalyst. This heat deterioration control means When it did not operate when the heat deterioration degree judged by said heat deterioration judging means was below predetermined level, but said predetermined level is exceeded and it is made to operate, progress of the heat deterioration after the heat deterioration degree of an occlusion reduction type NO_x catalyst reached said predetermined level can be controlled.

[Translation done.]

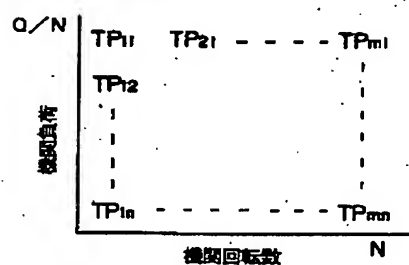
* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

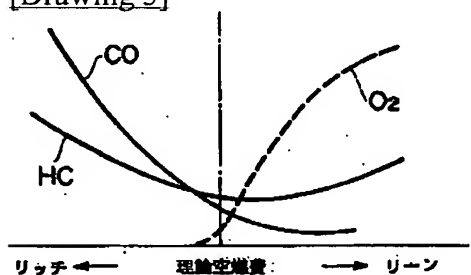
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

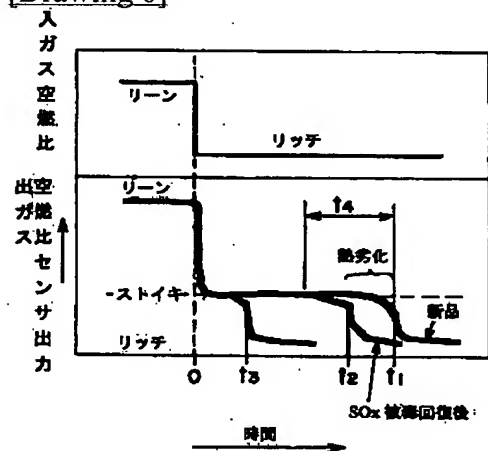
[Drawing 2]



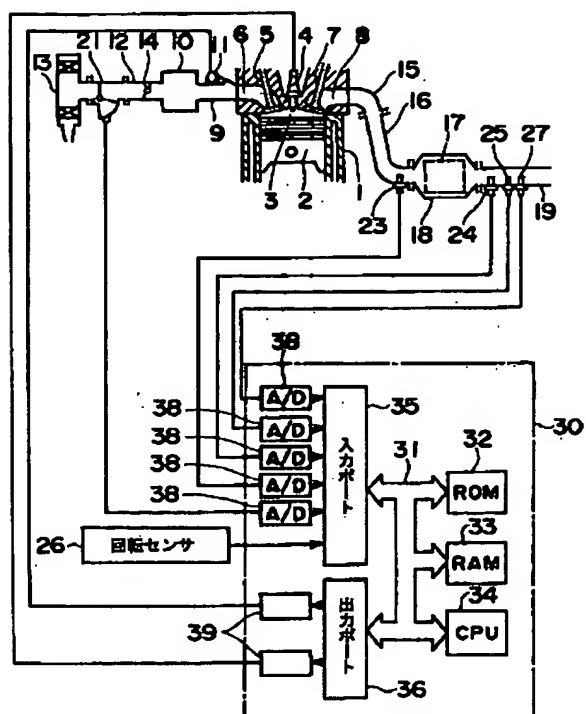
[Drawing 3]



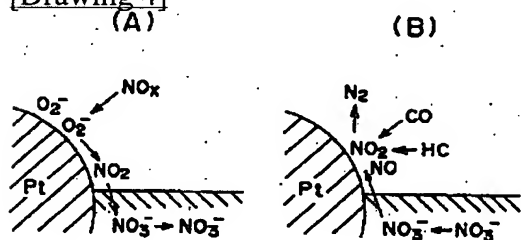
[Drawing 6]



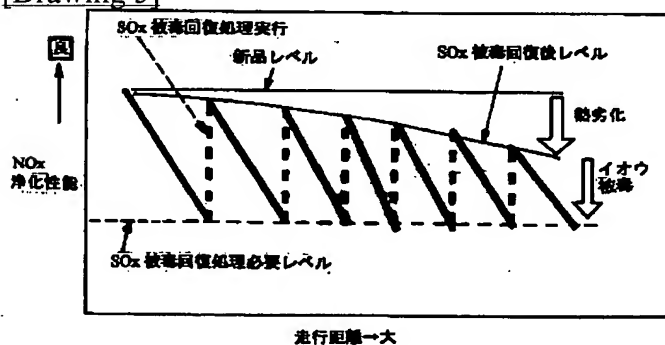
[Drawing 1]



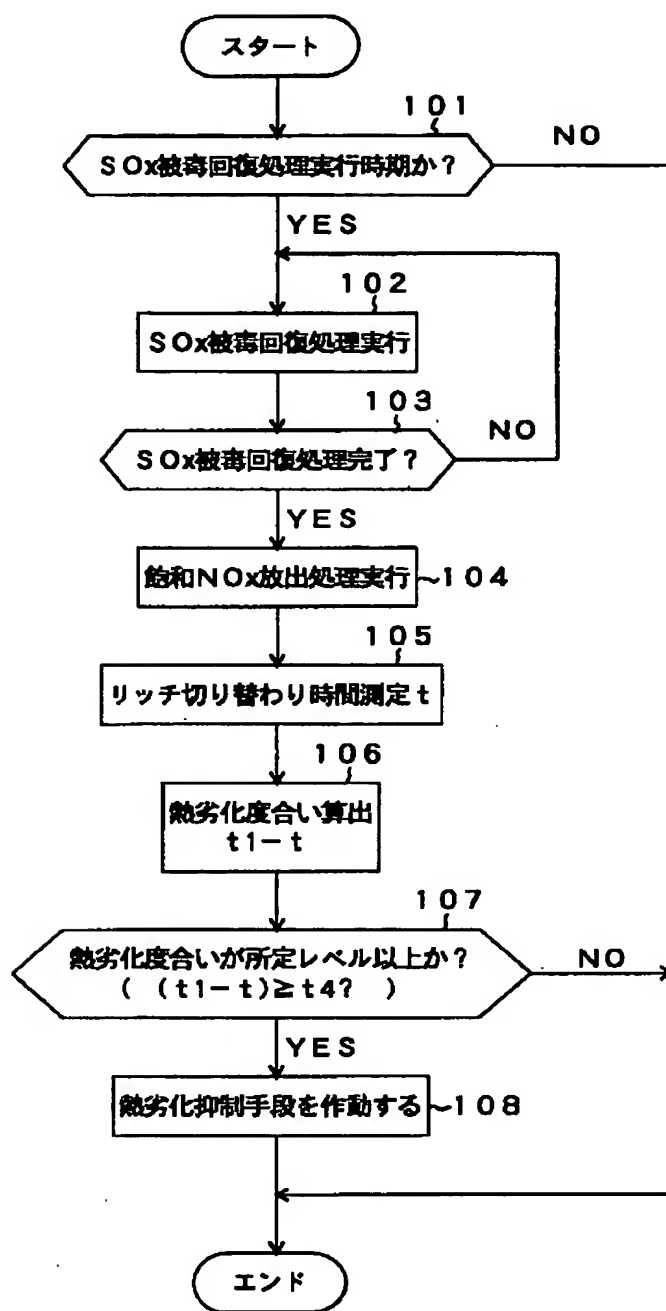
[Drawing 4]



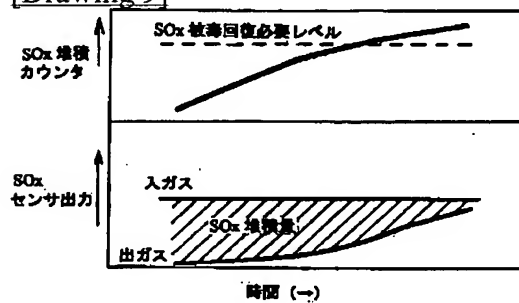
[Drawing 5]



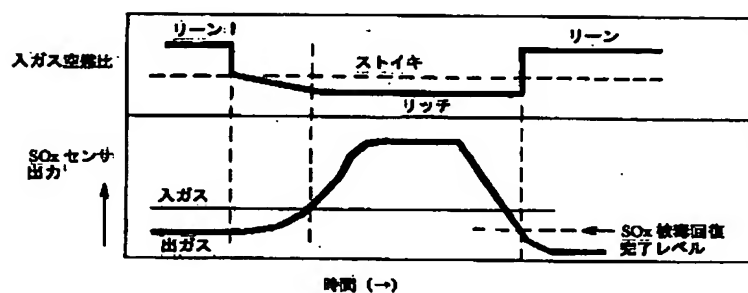
[Drawing 7]



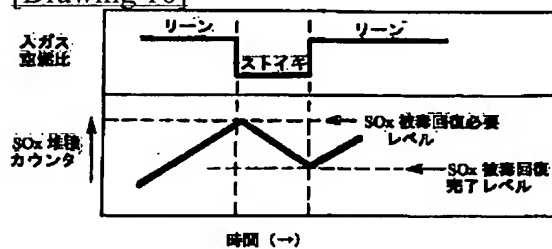
[Drawing 9]



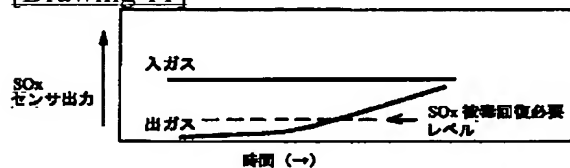
[Drawing 8]



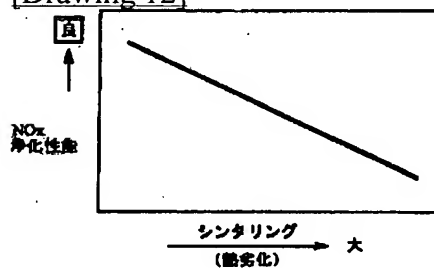
[Drawing 10]



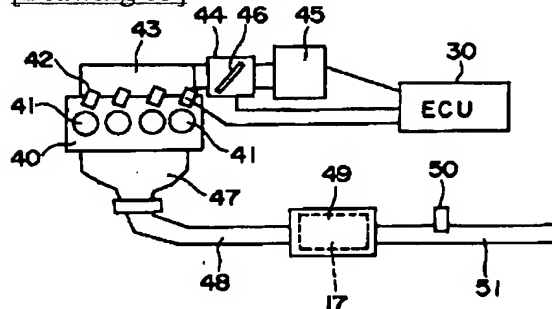
[Drawing 11]



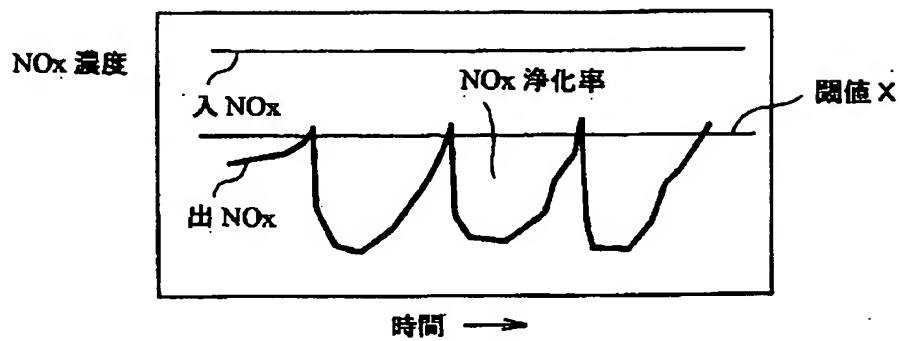
[Drawing 12]



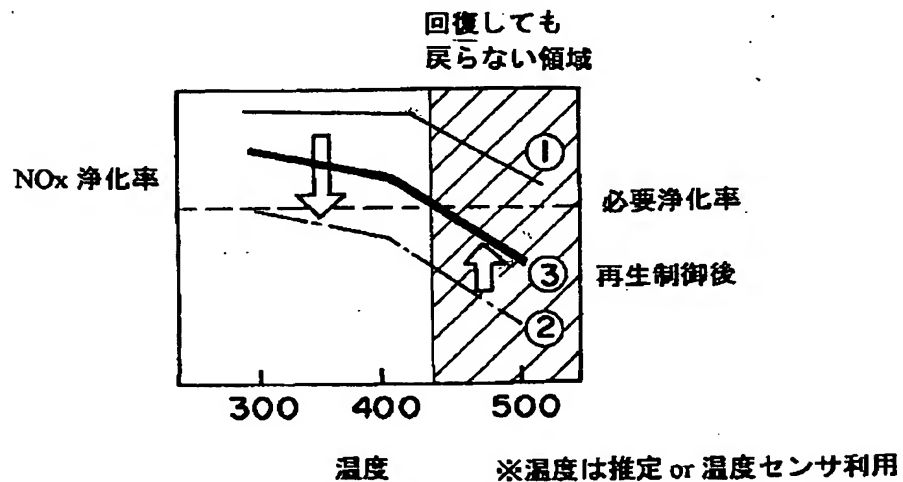
[Drawing 13]



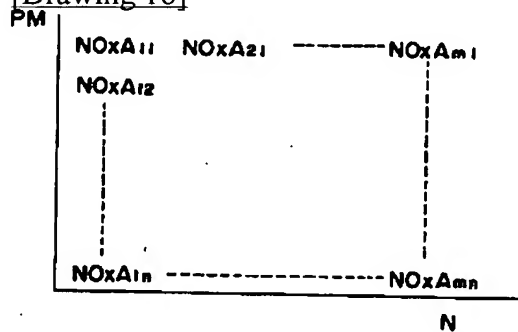
[Drawing 14]



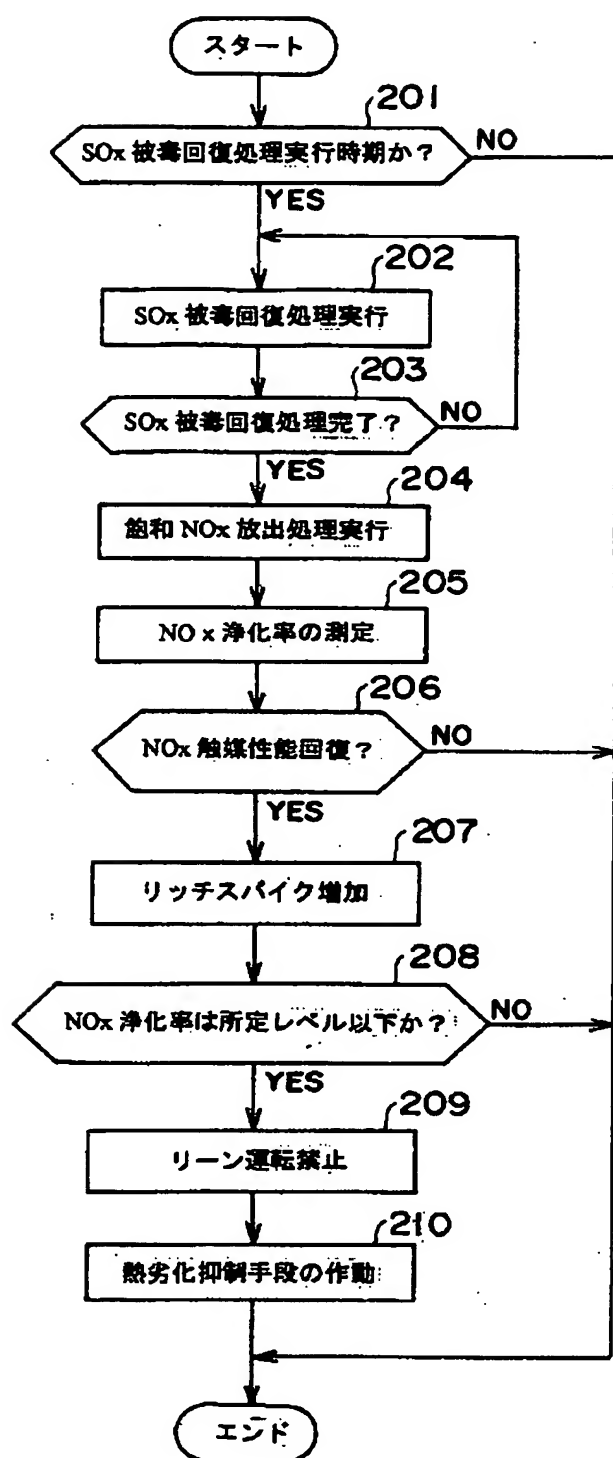
[Drawing 15]



[Drawing 16]



[Drawing 17]



[Translation done.]

(19)



JAPANESE PATENT OFFICE

PATENT ABSTRACTS OF JAPAN

(11) Publication number: **2001303937 A**

(43) Date of publication of application: **31.10.01**

(51) Int. Cl. **F01N 3/20**
B01D 53/94
F01N 3/08
F02D 41/04
F02D 41/12
F02D 45/00

(21) Application number: **2000275725**

(22) Date of filing: **11.09.00**

(30) Priority: **18.02.00 JP 2000040837**

(71) Applicant: **TOYOTA MOTOR CORP**

(72) Inventor: **ASANUMA TAKAMITSU**
TANAKA TOSHIKI

(54) **EXHAUST EMISSION CONTROL DEVICE FOR
INTERNAL COMBUSTION ENGINE**

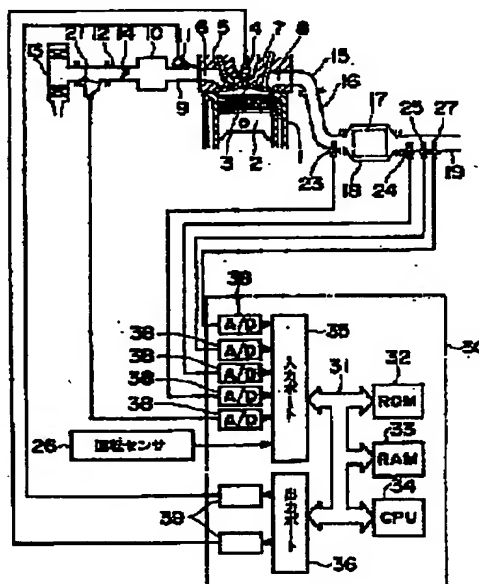
(57) Abstract

PROBLEM TO BE SOLVED: To detect the degree of thermal deterioration of a storage and reduction type NOx catalyst.

SOLUTION: This exhaust emission control device for an internal combustion engine having the storage and reduction type NOx catalyst 17 in an exhaust pipe 16 for the lean-combustible internal combustion engine comprises an incoming gas SOx sensor 23 provided at the upstream side of the NOx catalyst 17 and an outgoing gas SOx sensor 24 and an air/fuel ratio sensor 27 at the downstream side. SOx poisoning recovery treatment is executed to the NOx catalyst 17, and right after almost complete poisoning recovery, saturated NOx release treatment is executed to the NOx catalyst 17 and a change-to-rich time is measured and compared with a change-to-rich time for a new NOx catalyst 17 for judging the degree of thermal deterioration in accordance with the comparison value. Otherwise, the NOx clean-up rate of the NOx catalyst is measured for judging the degree of thermal

deterioration. When the degree of thermal deterioration exceeds a preset level, thermal deterioration inhibiting means is operated for inhibiting further thermal deterioration.

COPYRIGHT: (C)2001,JPO



(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2001-303937

(P2001-303937A)

(43) 公開日 平成13年10月31日 (2001. 10. 31)

(51) Int.Cl. ⁷	識別記号	F I	テーマコード(参考)
F 0 1 N 3/20	Z A B	F 0 1 N 3/20	Z A B C 3 G 0 8 4
			E 3 G 0 9 1
B 0 1 D 53/94		3/08	A 3 G 3 0 1
F 0 1 N 3/08		F 0 2 D 41/04	3 0 5 G 4 D 0 4 8
F 0 2 D 41/04	3 0 5		3 0 5 A
審査請求 未請求 請求項の数15 O L (全 20 頁) 最終頁に続く			

(21) 出願番号 特願2000-275725(P2000-275725)

(22) 出願日 平成12年9月11日(2000. 9. 11)

(31) 優先権主張番号 特願2000-40837(P2000-40837)

(32) 優先日 平成12年2月18日(2000. 2. 18)

(33) 優先権主張国 日本 (J P)

(71) 出願人 000003207

トヨタ自動車株式会社

愛知県豊田市トヨタ町1番地

(72) 発明者 浅沼 孝充

愛知県豊田市トヨタ町1番地 トヨタ自動車株式会社内

(72) 発明者 田中 俊明

愛知県豊田市トヨタ町1番地 トヨタ自動車株式会社内

(74) 代理人 100089244

弁理士 遠山 勉 (外3名)

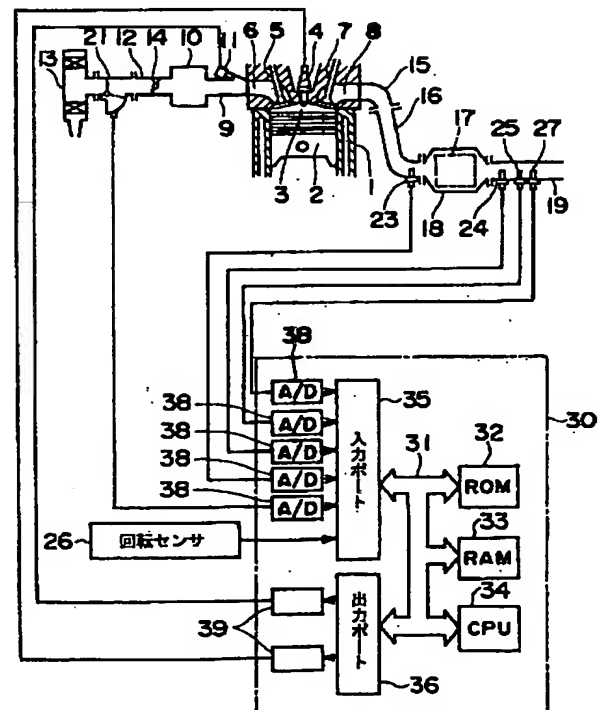
最終頁に続く

(54) 【発明の名称】 内燃機関の排気浄化装置

(57) 【要約】

【課題】 吸蔵還元型NO_x触媒の熱劣化度合いを検出する。

【解決手段】 希薄燃焼可能な内燃機関の排気管16に吸蔵還元型NO_x触媒17を備えた内燃機関の排気浄化装置において、NO_x触媒17の上流に入ガスSO_xセンサ23を設け、下流に出ガスSO_xセンサ24および空燃比センサ27を設ける。NO_x触媒17に対してSO_x被毒回復処理を実行し、ほぼ完全に被毒回復を行った直後に、NO_x触媒17に対して飽和NO_x放出処理を実行し、リッチ切り替わり時間を測定し、これと新品時のNO_x触媒17のリッチ切り替わり時間と比較して、その比較値に基づいて熱劣化度合いを判定する。またはNO_x触媒のNO_x浄化率を測定して熱劣化度合いを判定する。熱劣化度合いが所定レベルを越えたときには、熱劣化抑制手段を作動し、これ以後の熱劣化を抑制する。



【特許請求の範囲】

【請求項1】 (イ) 希薄燃焼可能な内燃機関の排気通路に設けられ、流入する排気ガスの空燃比がリーンのとときにNO_xを吸収し流入する排気ガスの酸素濃度が低いときに吸収したNO_xを放出しN₂に還元する吸蔵還元型NO_x触媒と、(ロ) 前記吸蔵還元型NO_x触媒からSO_xを放出させるSO_x被毒回復処理を実行する時期か否かを判定する被毒回復実行時期判定手段と、(ハ) 前記被毒回復実行時期判定手段により実行時期であると判定されたときに、前記吸蔵還元型NO_x触媒に堆積しているSO_xのほぼ全量を放出せしめて該吸蔵還元型NO_x触媒をSO_x被毒から回復させる被毒回復手段と、(ニ) 前記吸蔵還元型NO_x触媒のNO_x吸蔵能力を検出する吸蔵能力検出手段と、(ホ) 前記被毒回復手段によりSO_x被毒回復処理を実行した後に前記吸蔵能力検出手段によって検出された前記吸蔵還元型NO_x触媒のNO_x吸蔵能力と基準となるNO_x吸蔵能力とを比較し、その比較値に基づいて該吸蔵還元型NO_x触媒の熱劣化度合いを判定する熱劣化判定手段と、
を備えることを特徴とする内燃機関の排気浄化装置。

【請求項2】 前記吸蔵能力検出手段は、吸蔵還元型NO_x触媒のNO_x吸蔵状態を飽和状態にした後、該吸蔵還元型NO_x触媒へ流入する排気ガスの空燃比をリーンからリッチに切り替えてリッチに維持し、この空燃比の切り替えから該吸蔵還元型NO_x触媒の出口の排気ガスの空燃比がリッチになるまでの所要時間をNO_x吸蔵能力のパロメータとすることを特徴とする請求項1に記載の内燃機関の排気浄化装置。

【請求項3】 前記被毒回復実行時期判定手段は、前記吸蔵能力検出手段によって検出された吸蔵還元型NO_x触媒のNO_x吸蔵能力が所定の下限値を下回ったときにSO_x被毒回復処理の実行時期であると判定することを特徴とする請求項1または2に記載の内燃機関の排気浄化装置。

【請求項4】 (イ) 希薄燃焼可能な内燃機関の排気通路に設けられ、流入する排気ガスの空燃比がリーンのとときにNO_xを吸収し流入する排気ガスの酸素濃度が低いときに吸収したNO_xを放出しN₂に還元する吸蔵還元型NO_x触媒と、(ロ) 前記吸蔵還元型NO_x触媒からSO_xを放出させるSO_x被毒回復処理を実行する時期か否かを判定する被毒回復実行時期判定手段と、(ハ) 前記被毒回復実行時期判定手段により実行時期であると判定されたときに、前記吸蔵還元型NO_x触媒に堆積しているSO_xのほぼ全量を放出せしめて該吸蔵還元型NO_x触媒をSO_x被毒から回復させる被毒回復手段と、(ニ) 前記吸蔵還元型NO_x触媒のNO_x浄化率を測定する浄化率測定手段と、(ホ) 前記被毒回復手段によりSO_x被毒回復処理を実行した後に前記浄化率測定によって測定された前記吸蔵還元型NO_x触媒のNO_x浄化率基準となるNO_x浄化率を比較し、その比較値に基づいて該吸蔵還

元型NO_x触媒の熱劣化度合いを判定する熱劣化判定手段と、

を備えることを特徴とする内燃機関の排気浄化装置。

【請求項5】 前記NO_x浄化率測定手段は、NO_x触媒に流入する排気ガス中のNO_x量と、NO_x触媒の下流に設置したNO_x検出手段による排気ガス中のNO_x量に基づいてNO_x浄化率を測定することを特徴とする請求項3または2に記載の内燃機関の排気浄化装置。

【請求項6】 前記被毒回復実行時期判定手段は、前記浄化率測定手段によって測定された吸蔵還元型NO_x触媒のNO_x浄化率が所定の下限値を下回ったときにSO_x被毒回復処理の実行時期であると判定することを特徴とする請求項3または4に記載の内燃機関の排気浄化装置。

【請求項7】 前記吸蔵還元型NO_x触媒に流入する排気ガスのSO_x濃度を検出する入ガスSO_x濃度検出手段を備え、

前記被毒回復実行時期判定手段は、前記入ガスSO_x濃度検出手段により検出されたSO_x濃度と前記内燃機関の吸入空気量に基づいて算出された吸蔵還元型NO_x触媒に流入するSO_x量が所定量を越えたときに、SO_x被毒回復処理の実行時期であると判定することを特徴とする請求項1から6のいずれかに記載の内燃機関の排気浄化装置。

【請求項8】 前記吸蔵還元型NO_x触媒に流入する排気ガスのSO_x濃度を検出する入ガスSO_x濃度検出手段を備え、

前記被毒回復実行時期判定手段は、前記入ガスSO_x濃度検出手段により検出されたSO_x濃度から推定した前記内燃機関の燃料の硫黄濃度と燃料消費量または走行距離に基づいて算出された吸蔵還元型NO_x触媒に流入するSO_x量が所定量を越えたときに、SO_x被毒回復処理の実行時期であると判定することを特徴とする請求項1から6のいずれかに記載の内燃機関の排気浄化装置。

【請求項9】 前記吸蔵還元型NO_x触媒に流入する排気ガスのSO_x濃度を検出する入ガスSO_x濃度検出手段と、該吸蔵還元型NO_x触媒から流出する排気ガスのSO_x濃度を検出する出ガスSO_x濃度検出手段とを備え、前記被毒回復実行時期判定手段は、前記入ガスSO_x濃度検出手段により検出されたSO_x濃度と前記出ガスSO_x濃度検出手段により検出されたSO_x濃度との濃度差と前記内燃機関の吸入空気量あるいは排気ガス量に基づいて推定されるSO_x吸蔵量が所定量を越えたときに、SO_x被毒回復処理の実行時期であると判定することを特徴とする請求項1から6のいずれかに記載の内燃機関の排気浄化装置。

【請求項10】 前記吸蔵還元型NO_x触媒に流入する排気ガスのSO_x濃度を検出する入ガスSO_x濃度検出手段と、該吸蔵還元型NO_x触媒から流出する排気ガスのSO_x濃度を検出する出ガスSO_x濃度検出手段とを備

え、
前記被毒回復実行時期判定手段は、前記出ガスSOx濃度検出手段により検出されたSOx濃度が前記入ガスSOx濃度検出手段により検出されたSOx濃度に対して所定レベルまで接近したときに、SOx被毒回復処理の実行時期であると判定することを特徴とする請求項1から6のいずれかに記載の内燃機関の排気浄化装置。

【請求項11】 前記吸蔵還元型NOx触媒に吸蔵されたと推定されるSOx吸蔵量から、前記被毒回復手段によりSOx被毒回復処理を実行しているときの前記出ガスSOx濃度検出手段により検出されたSOx濃度と前記入ガスSOx濃度検出手段により検出されたSOx濃度との濃度差と前記内燃機関の吸入空気量あるいは排気ガス量に基づいて推定される放出SOx量を減算して、吸蔵還元型NOx触媒に残存するSOx量を推定し、このSOx残存量が所定量まで減少したときに、前記被毒回復手段によるSOx被毒回復処理を終了することを特徴とする請求項9に記載の内燃機関の排気浄化装置。

【請求項12】 前記吸蔵還元型NOx触媒の熱劣化を抑制する熱劣化抑制手段を備え、この熱劣化抑制手段は、前記熱劣化判定手段により判定された熱劣化度合いが所定レベル以下のときには作動されず、前記所定レベルを超えたときに作動されることを特徴とする請求項1から6のいずれかに記載の内燃機関の排気浄化装置。

【請求項13】 前記熱劣化抑制手段は、内燃機関の高温運転域でのフューエルカットを禁止するフューエルカット禁止制御であることを特徴とする請求項12に記載の内燃機関の排気浄化装置。

【請求項14】 前記熱劣化抑制手段は、内燃機関の高温運転域におけるリーン運転領域を減少するリーン運転領域減少制御であることを特徴とする請求項12に記載の内燃機関の排気浄化装置。

【請求項15】 前記熱劣化抑制手段は、熱劣化の度合いに応じてNOx触媒に流入させるリッチまたはストイキの排気ガス量を増大させ、または／及びリッチまたはストイキの排気ガスをNOx触媒に流入させる周期を短くすることを特徴とする請求項12に記載の内燃機関の排気浄化装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、希薄燃焼可能な内燃機関より排出される排気ガスから窒素酸化物(NOx)を浄化することができる排気浄化装置に係り、特にNOx触媒の熱劣化を検出することができるものに関する。

【0002】

【従来の技術】希薄燃焼可能な内燃機関より排出される排気ガスからNOxを浄化する排気浄化装置として、吸蔵還元型NOx触媒がある。吸蔵還元型NOx触媒(以下、単に触媒あるいはNOx触媒ということもある)

は、流入排気ガスの空燃比がリーン(即ち、酸素過剰雰囲気下)のときにNOxを吸収し、流入排気ガスの酸素濃度が低下したときに吸収したNOxを放出しN₂に還元する触媒である。

【0003】NOx触媒の構造、およびNOx浄化のメカニズムについて簡単に説明すると、NOx触媒は、アルミナなどの担体上に、白金(Pt)などの触媒物質とバリウム(Ba)などのNOx吸蔵剤を担持してなり(以下の説明では、PtとBaが担持されてなるNOx触媒の例で説明する)、NOx触媒にリーン空燃比の排気ガスが流入すると、排気ガス中のNOxはPtの表面で酸化されてNO₂になり、このNO₂がBa内に吸収されてBaOと結合し、硝酸イオンNO₃⁻の形で吸収される。このNOxの吸収はBaとPtとの界面において行われる。一方、NOx触媒にストイキ(理論空燃比)またはリッチ空燃比の排気ガスが流入して酸素濃度が低下すると、NOx触媒に吸収されていたNO₃⁻がNO₂あるいはNOの形で放出され、さらに排気ガス中のHCやCOと反応してN₂に還元せしめられる。

【0004】したがって、このNOx触媒を希薄燃焼可能な内燃機関の排気通路に配置し、リーン空燃比の排気ガスと、ストイキまたはリッチ空燃比の排気ガスを交互に流すと、排気ガス中のNOxを浄化することができる。

【0005】このNOx触媒を排気ガス浄化に長期に使用していると、このNOx触媒は経時劣化し、図5に示すようにNOx浄化能力が低下していくことが知られている。この劣化は(a)燃料中の硫黄と(b)熱に原因があると考えられており、燃料中の硫黄に起因する劣化を硫黄被毒劣化といい、熱に起因する劣化を熱劣化といって区別することもある。なお、硫黄被毒劣化はS被毒劣化あるいはSOx被毒劣化と表現することもあるが、以下の説明ではSOx被毒劣化という表現で統一する。

【0006】SOx被毒劣化について説明すると、一般に、内燃機関の燃料には硫黄分が含まれており、内燃機関で燃料を燃焼すると、燃料中の硫黄分が燃焼してSO₂やSO₃などの硫黄酸化物(SOx)が発生する。前記吸蔵還元型NOx触媒は、NOxの吸収作用を行うのと同じメカニズムで排気ガス中のSOxの吸収を行うので、内燃機関の排気通路にNOx触媒を配置すると、このNOx触媒にはNOxのみならずSOxも吸収される。

【0007】ところが、前記NOx触媒に吸収されたSOxは時間経過とともに安定な硫酸塩を形成するため、分解、放出されにくく触媒内に蓄積され易い傾向がある。NOx触媒に硫酸塩が蓄積されることをSOx被毒といい、SOx被毒が進行してNOx触媒内のSOx蓄積量が増大すると、触媒のNOx吸収容量が減少するためNOx浄化率が低下する。これがSOx被毒劣化である。

【0008】熱劣化について説明すると、前述したように、NOx触媒におけるNOxの吸収はPt(触媒物質)

とBa(Nox吸収剤)との界面において行われるが、Ptは熱によってシタリングを起こし、成長して粒径が大きくなることが知られている。車両用内燃機関から排出される排気ガスの浄化においては、Nox触媒に加わる熱負荷が大きく、Ptのシタリングを避けることはできない。このようにPtがシタリングを起こすと、PtとBaの接触面積が少なくなり、即ち、PtとBaの界面が少なくなる。その結果、Nox触媒のNox吸収能力が低下し、Nox浄化能力が低下する。これが熱劣化である。

【0009】図12は、触媒物質のシタリング(触媒物質の粒径成長)がNox浄化性能に与える影響を示しており、触媒物質のシタリングが進んでいないとき(即ち、粒径が小さいとき)にはNox浄化性能が高く、シタリングが進むにしたがって(即ち、粒径が大きくなるにしたがって)Nox浄化性能が低下する。

【0010】

【発明が解決しようとする課題】ところで、前記SOx被毒劣化については、特許番号第2745985号の特許公報等に開示されているように、所定の回復処理を施すことによって、Nox触媒に吸収されているSOxを放出させSO₂に還元することができるので、Nox触媒をSOx被毒から回復させることが可能である。

【0011】これに対して、一度シタリングを起こしたPtをシタリングする前の状態に戻すことは不可能であり、したがって、Nox触媒を熱劣化から回復させることは不可能である。そのため、Nox触媒を管理する上で、Nox触媒の熱劣化の度合い(熱劣化レベル)を検出することは重要な意味がある。

【0012】しかしながら、現在のところ熱劣化度合いを検出する技術は確立されておらず、熱劣化の度合いを検出する技術の開発が切望されている。本発明はこのような従来の技術の問題点を鑑みてなされたものであり、本発明が解決しようとする課題は、吸蔵還元型Nox触媒の熱劣化度合いの検出技術を確立することにより、内燃機関の排気浄化技術の向上を図ることにある。

【0013】

【課題を解決するための手段】本発明は前記課題を解決するために、以下の手段を採用した。第1の発明にかかる内燃機関の排気浄化装置は、(イ)希薄燃焼可能な内燃機関の排気通路に設けられ、流入する排気ガスの空燃比がリーンのときにNoxを吸収し流入する排気ガスの酸素濃度が低いときに吸収したNoxを放出しN₂に還元する吸蔵還元型Nox触媒と、(ロ)前記吸蔵還元型Nox触媒からSOxを放出させるSOx被毒回復処理を実行する時期か否かを判定する被毒回復実行時期判定手段と、(ハ)前記被毒回復実行時期判定手段により実行時期であると判定されたときに、前記吸蔵還元型Nox触媒に堆積しているSOxのほぼ全量を放出せしめて該吸蔵還元型Nox触媒をSOx被毒から回復させる被毒回

復手段と、(ニ)前記吸蔵還元型Nox触媒のNox吸蔵能力を検出する吸蔵能力検出手段と、(ホ)前記被毒回復手段によりSOx被毒回復処理を実行した後に前記吸蔵能力検出手段によって検出された前記吸蔵還元型Nox触媒のNox吸蔵能力と基準となるNox吸蔵能力とを比較し、その比較値に基づいて該吸蔵還元型Nox触媒の熱劣化度合いを判定する熱劣化判定手段と、を備えることを特徴とする。

【0014】この内燃機関の排気浄化装置では、被毒回復実行時期判定手段が、吸蔵還元型Nox触媒に対してSOx被毒回復処理を実行すべき時期であると判定すると、被毒回復手段が、吸蔵還元型Nox触媒に対するSOx被毒回復処理を実行し、吸蔵還元型Nox触媒に吸蔵されているSOxをほぼ完全に放出する。そして、SOx被毒回復処理の完了直後に、吸蔵能力検出手段は吸蔵還元型Nox触媒のNox吸蔵能力を検出する。この後、熱劣化判定手段が、吸蔵能力検出手段によって検出されたNox吸蔵能力と基準となるNox吸蔵能力とを比較し、その比較値に基づいて吸蔵還元型Nox触媒の熱劣化度合いを判定する。

【0015】熱劣化度合いの判定原理は次の通りである。吸蔵還元型Nox触媒の劣化には、燃料中の硫黄に起因するSOx被毒劣化と、熱に起因する熱劣化があるが、SOx被毒劣化は所定の被毒回復処理を実行すれば回復することができるのに対して、熱劣化は一旦生じてしまうと回復することができない。したがって、SOx被毒回復処理を実行してもなお性能回復不能な部分は熱劣化によるものとみなすことができる。これが本発明における熱劣化度合い判定の原理である。

【0016】第1の発明にかかる内燃機関の排気浄化装置において、前記熱劣化判定手段が基準とするNox吸蔵能力は、SOx被毒劣化および熱劣化のいずれも受けていない新品の吸蔵還元型Nox触媒のNox吸蔵能力とすることができる。

【0017】前記熱劣化判定手段が、前記吸蔵能力検出手段によって検出された前記吸蔵還元型Nox触媒のNox吸蔵能力と基準となるNox吸蔵能力とを比較して求める比較値は、両者の差としてもよいし、一方を他方で除した商としてもよい。

【0018】また第2の発明にかかる内燃機関の排気浄化装置は、(イ)希薄燃焼可能な内燃機関の排気通路に設けられ、流入する排気ガスの空燃比がリーンのときにNoxを吸収し流入する排気ガスの酸素濃度が低いときに吸収したNoxを放出しN₂に還元する吸蔵還元型Nox触媒と、(ロ)前記吸蔵還元型Nox触媒からSOxを放出させるSOx被毒回復処理を実行する時期か否かを判定する被毒回復実行時期判定手段と、(ハ)前記被毒回復実行時期判定手段により実行時期であると判定されたときに、前記吸蔵還元型Nox触媒に堆積しているSOxのほぼ全量を放出せしめて該吸蔵還元型Nox触媒を

SO_x被毒から回復させる被毒回復手段と、(二)前記吸蔵還元型NO_x触媒のNO_x浄化率を測定する浄化率測定手段と、(ホ)前記被毒回復手段によりSO_x被毒回復処理を実行した後に前記浄化率測定によって測定された前記吸蔵還元型NO_x触媒のNO_x浄化率基準となるNO_x浄化率を比較し、その比較値に基づいて該吸蔵還元型NO_x触媒の熱劣化度合いを判定する熱劣化判定手段と、を備えることを特徴とする

【0019】第2の発明では、前記NO_x浄化率測定手段は、NO_x触媒に流入する排気ガス中のNO_x量と、NO_x触媒の下流に設置したNO_x検出手段による排気ガス中のNO_x量に基づいてNO_x浄化率を測定することができる。第2の発明の内燃機関の排気浄化装置では、被毒回復実行時期判定手段が、吸蔵還元型NO_x触媒に対してSO_x被毒回復処理を実行すべき時期であると判定すると、被毒回復手段が、吸蔵還元型NO_x触媒に対するSO_x被毒回復処理を実行し、吸蔵還元型NO_x触媒に吸蔵されているSO_xをほぼ完全に放出する。そして、SO_x被毒回復処理の完了直後に、浄化率測定手段は吸蔵還元型NO_x触媒のNO_x浄化率を測定する。この後、熱劣化判定手段が、浄化率測定手段によって測定されたNO_x浄化率と基準となるNO_x浄化率とを比較し、その比較値に基づいて吸蔵還元型NO_x触媒の熱劣化度合いを判定する。

【0020】熱劣化度合いの判定原理は次の通りである。吸蔵還元型NO_x触媒の劣化には、燃料中の硫黄に起因するSO_x被毒劣化と、熱に起因する熱劣化があるが、SO_x被毒劣化は所定の被毒回復処理を実行すれば回復することができるのに対して、熱劣化は一旦生じてしまうと回復することができない。したがって、SO_x被毒回復処理を実行してもなお性能回復不能な部分は熱劣化によるものとみなすことができる。これが本発明における熱劣化度合い判定の原理である。

【0021】第2の発明にかかる内燃機関の排気浄化装置において、前記熱劣化判定手段が基準とするNO_x浄化率は、SO_x被毒劣化および熱劣化のいずれも受けていない新品の吸蔵還元型NO_x触媒のNO_x浄化率とすることができる。

【0022】前記熱劣化判定手段が、前記浄化率測定手段によって測定された前記吸蔵還元型NO_x触媒のNO_x浄化率と基準となるNO_x浄化率とを比較して求める比較値は、両者の差としてもよいし、一方を他方で除した商としてもよい。

【0023】第1及び第2の発明(以下、本発明)における希薄燃焼可能な内燃機関としては、筒内直接噴射式のリーンバーンガソリンエンジンやディーゼルエンジンを例示することができる。排気ガスの空燃比とは、機関吸気通路及び吸蔵還元型NO_x触媒よりも上流での排気通路内に供給された空気及び燃料(炭化水素)の比をいう。

【0024】内燃機関がリーンバーンガソリンエンジンの場合には、排気空燃比制御手段は、燃焼室に供給される混合気空燃比を制御することにより排気ガスの空燃比を制御することができる。また、内燃機関がディーゼルエンジンの場合には、吸気行程または膨張行程または排気行程で燃料を噴射する所謂副噴射により、あるいは、吸蔵還元型NO_x触媒よりも上流の排気通路内に還元剤を供給することにより排気ガスの空燃比を制御することができる。

【0025】吸蔵還元型NO_x触媒は、流入する排気ガスの空燃比がリーンのときにNO_xを吸収し、流入する排気ガス中の酸素濃度が低下すると吸収したNO_xを放出し、N₂に還元する触媒である。この吸蔵還元型NO_x触媒は、例えばアルミナを担体とし、この担体上に例えばカリウムK、ナトリウムNa、リチウムLi、セシウムCsのようなアルカリ金属、バリウムBa、カルシウムCaのようなアルカリ土類、ランタンLa、イットリウムYのような希土類から選ばれた少なくとも一つと、白金Ptのような貴金属とが担持されてなる。

【0026】また前記吸蔵能力検出手段は、吸蔵還元型NO_x触媒のNO_x吸蔵状態を飽和状態にした後、該吸蔵還元型NO_x触媒へ流入する排気ガスの空燃比をリーンからリッチに切り替えてリッチに維持し、この空燃比の切り替えから該吸蔵還元型NO_x触媒の出口の排気ガスの空燃比がリッチになるまでの所要時間をNO_x吸蔵能力のパロメータとして検出することができる。

【0027】本発明にかかる内燃機関の排気浄化装置において、前記被毒回復実行時期判定手段は、前記吸蔵能力検出手段によって検出された吸蔵還元型NO_x触媒のNO_x吸蔵能力が所定の下限値を下回ったときにSO_x被毒回復処理の実行時期であると判定することができる。この場合には、例えば、一定の燃料消費量毎あるいは一定の走行距離毎に吸蔵能力検出手段によって吸蔵還元型NO_x触媒のNO_x吸蔵能力を検出するのが好ましい。

【0028】また前記吸蔵還元型NO_x触媒に流入する排気ガスのSO_x濃度を検出する入ガスSO_x濃度検出手段を備え、前記被毒回復実行時期判定手段は、前記入ガスSO_x濃度検出手段により検出されたSO_x濃度と前記内燃機関の吸入空気量に基づいて算出された吸蔵還元型NO_x触媒に流入するSO_x量が所定量を越えたときに、SO_x被毒回復処理の実行時期であると判定することができる。

【0029】さらに前記吸蔵還元型NO_x触媒に流入する排気ガスのSO_x濃度を検出する入ガスSO_x濃度検出手段を備え、前記被毒回復実行時期判定手段は、前記入ガスSO_x濃度検出手段により検出されたSO_x濃度から推定した前記内燃機関の燃料の硫黄濃度と燃料消費量または走行距離に基づいて算出された吸蔵還元型NO_x触媒に流入するSO_x量が所定量を越えたときに、SO_x被毒回復処理の実行時期であると判定することができる。

(以下の説明では、NO_x触媒と略する場合もある)を内蔵したケーシング18に接続され、ケーシング18は排気管19を介して図示しないマフラーに接続されている。

【0040】エンジンコントロール用の電子制御ユニット(ECU)30はデジタルコンピュータからなり、双方向バス31によって相互に接続されたROM(リードオンリメモリ)32、RAM(ランダムアクセスメモリ)33、CPU(セントラルプロセッサユニット)34、入力ポート35、出力ポート36を具備する。エアフロメータ21は吸入空気量に比例した出力電圧を発生し、この出力電圧がAD変換器38を介して入力ポート35に入力される。

【0041】ケーシング18の上流の排気管16には、NO_x触媒17に流入する排気ガス(以下、これを入ガスという)のSO_x濃度に比例した出力電圧を発生する入ガスSO_xセンサ(入ガスSO_x濃度検出手段)23が設けられている。一方、ケーシング18の下流の排気管19には、NO_x触媒17から流出する排気ガス(以下、これを出ガスという)のSO_x濃度に比例した出力電圧を発生する出ガスSO_xセンサ(出ガスSO_x濃度検出手段)24と、出ガスの温度に比例した出力電圧を発生する温度センサ25と、出ガスの空燃比を表す出力電圧を発生する空燃比センサ27とが取り付けられている。これらSO_xセンサ23、24、温度センサ25、空燃比センサ27の出力電圧はそれぞれ対応するAD変換器38を介して入力ポート35に入力される。

【0042】また、入力ポート35には機関回転数を表す出力パルスを発生する回転数センサ26が接続されている。出力ポート36は対応する駆動回路39を介して夫々点火栓4および燃料噴射弁11に接続されている。

【0043】このガソリンエンジンでは、例えば次式に基づいて燃料噴射時間TAUが算出される。

$$TAU = TP \cdot K$$

ここで、TPは基本燃料噴射時間を示しており、Kは補正係数を示している。基本燃料噴射時間TPは機関シリンダ内に供給される混合気空燃比を理論空燃比とするのに必要な燃料噴射時間を示している。この基本燃料噴射時間TPは予め実験により求められ、機関負荷Q/N(吸入空気量Q/機関回転数N)および機関回転数Nの関数として図2に示すようなマップの形で予めROM32内に記憶されている。補正係数Kは機関シリンダ内に供給される混合気空燃比を制御するための係数であって、K=1.0であれば機関シリンダ内に供給される混合気は理論空燃比となる。これに対してK<1.0になれば機関シリンダ内に供給される混合気空燃比は理論空燃比よりも大きくなり、即ちリーンとなり、K>1.0になれば機関シリンダ内に供給される混合気空燃比は理論空燃比よりも小さくなり、即ちリッチとなる。

【0044】そして、この実施の形態のガソリンエン

ンでは、機関低中負荷運転領域では補正係数Kの値が1.0よりも小さい値とされてリーン空燃比制御が行われ、機関高負荷運転領域、エンジン始動時の暖機運転時、加速時、高速の定速運転時では補正係数Kの値が1.0とされてストイキ制御が行われ、機関全負荷運転領域では補正係数Kの値は1.0よりも大きな値とされてリッチ空燃比制御が行われるように設定してある。

【0045】内燃機関では通常、低中負荷運転される頻度が最も高く、したがって運転期間中の大部分において補正係数Kの値が1.0よりも小さくされて、リーン混合気が燃焼せしめられることになる。

【0046】図3は燃焼室3から排出される排気ガス中の代表的な成分の濃度を概略的に示している。この図からわかるように、燃焼室3から排出される排気ガス中の未燃HC、COの濃度は燃焼室3内に供給される混合気空燃比がリッチになるほど増大し、燃焼室3から排出される排気ガス中の酸素O₂の濃度は燃焼室3内に供給される混合気空燃比がリーンになるほど増大する。

【0047】ケーシング18内に收容されているNO_x触媒(吸蔵還元型NO_x触媒)17は、例えばアルミナを担体とし、この担体上に例えばカリウムK、ナトリウムNa、リチウムLi、セシウムCsのようなアルカリ金属、バリウムBa、カルシウムCaのようなアルカリ土類、ランタンLa、イットリウムYのような希土類から選ばれた少なくとも一つと、白金Ptのような貴金属とが担持されてなる。

【0048】このNO_x触媒17を機関の排気通路に配置すると、NO_x触媒17は、流入する排気ガス空燃比(以下、排気空燃比ということもある)がリーンのときにはNO_xを吸収し、流入排気ガス中の酸素濃度が低下すると吸収したNO_xを放出するNO_xの吸放出作用を行う。ここで、排気空燃比とは、機関吸気通路およびNO_x触媒17より上流の排気通路内に供給された空気および燃料(炭化水素)の比をいう。

【0049】なお、NO_x触媒17より上流の排気通路内に燃料(炭化水素)あるいは空気が供給されない場合には、排気空燃比は燃焼室3内に供給される混合気空燃比に一致し、したがってこの場合には、NO_x触媒17は燃焼室3内に供給される混合気空燃比がリーンのときにはNO_xを吸収し、燃焼室3内に供給される混合気中の酸素濃度が低下すると吸収したNO_xを放出することになる。

【0050】NO_x触媒17によるNO_xの吸放出作用は図4に示すようなメカニズムで行われているものと考えられる。以下、このメカニズムについて担体上に白金PtおよびバリウムBaを担持させた場合を例にとって説明するが、他の貴金属、アルカリ金属、アルカリ土類、希土類を用いても同様なメカニズムとなる。

【0051】まず、流入排気ガスがかなりリーンになると流入排気ガス中の酸素濃度が大幅に増大し、図4

(A) に示されるように酸素 O_2 が O_2^- 又は O^{2-} の形で白金Ptの表面に付着する。一方、流入排気ガスに含まれるNOは、白金Ptの表面上で O_2^- 又は O^{2-} と反応し、 NO_2 となる($2NO + O_2 \rightarrow 2NO_2$)。

【0052】次いで、生成された NO_2 の一部は、白金Pt上で酸化されつつBa内に吸収されて酸化バリウム BaO と結合しながら、図4(A)に示されるように硝酸イオン NO_3^- の形でBa内に拡散する。このようにして NO_x が NO_x 触媒17内に吸収される。

【0053】流入排気ガス中の酸素濃度が高い限り白金Ptの表面で NO_2 が生成され、 NO_x 触媒17の NO_x 吸収能力が飽和しない限り、 NO_2 が NO_x 触媒17内に吸収されて硝酸イオン NO_3^- が生成される。

【0054】これに対して、流入排気ガス中の酸素濃度が低下して NO_2 の生成量が低下すると反応が逆方向($NO_3^- \rightarrow NO_2$)に進み、Ba内の硝酸イオン NO_3^- が NO_2 またはNOの形でBaから放出される。即ち、流入排気ガス中の酸素濃度が低下すると、 NO_x 触媒17から NO_x が放出されることになる。図3に示されるように、流入排気ガスのリーンの度合いが低くなれば流入排気ガス中の酸素濃度が低下し、したがって流入排気ガスのリーンの度合いを低くすれば NO_x 触媒17から NO_x が放出されることとなる。

【0055】一方、このとき、燃焼室3内に供給される混合気がストイキまたはリッチ空燃比になると、図3に示されるように機関からは多量の未燃HC、COが排出され、これら未燃HC、COは、白金Pt上の酸素 O_2^- 又は O^{2-} と反応して酸化せしめられる。

【0056】また、排気空燃比が理論空燃比またはリッチ空燃比になると流入排気ガス中の酸素濃度が極度に低下するために NO_x 触媒17から NO_2 またはNOが放出され、この NO_2 またはNOは、図4(B)に示されるように未燃HC、COと反応して還元せしめられて N_2 となる。

【0057】即ち、流入排気ガス中のHC、COは、まず白金Pt上の酸素 O_2^- 又は O^{2-} とただちに反応して酸化せしめられ、次いで白金Pt上の酸素 O_2^- 又は O^{2-} が消費されてもまだHC、COが残っていれば、このHC、COによって NO_x 触媒17から放出された NO_x および流入排気ガス中の NO_x が N_2 に還元せしめられる。

【0058】このようにして白金Ptの表面上に NO_2 またはNOが存在しなくなると、 NO_x 触媒17から次から次へと NO_2 またはNOが放出され、さらに N_2 に還元せしめられる。したがって、排気空燃比を理論空燃比またはリッチにすると短時間の内に NO_x 触媒17から NO_x が放出されることになる。

【0059】このように、排気空燃比がリーンになると NO_x が NO_x 触媒17に吸収され、排気空燃比を理論空燃比あるいはリッチにすると NO_x が NO_x 触媒17から短時間のうちに放出され、 N_2 に還元される。したがっ

て、大気中への NO_x の排出を阻止することができる。

【0060】ところで、この実施の形態では前述したように、全負荷運転時には燃焼室3内に供給される混合気がリッチとされ、また高負荷運転時等には混合気が理論空燃比とされ、低中負荷運転時には混合気がリーンとされるので、低中負荷運転時に排気ガス中の NO_x が NO_x 触媒17に吸収され、全負荷運転時及び高負荷運転時等に NO_x 触媒17から NO_x が放出され還元されることになる。しかしながら、全負荷運転あるいは高負荷運転等の頻度が少なく、低中負荷運転の頻度が多くその運転時間が長ければ、 NO_x の放出・還元が間に合わなくなり、 NO_x 触媒17の NO_x の吸収能力が飽和して NO_x を吸収できなくなってしまう。

【0061】そこで、この実施の形態では、リーン混合気の燃焼が行われている場合、即ち中低負荷運転を行っているときには、比較的短い周期でスパイク的(短時間)にストイキまたはリッチ混合気の燃焼が行われるように混合気空燃比を制御し、短周期的に NO_x の放出・還元を行っている。このように NO_x の吸放出のために、排気空燃比(この実施の形態では混合気空燃比)が比較的短い周期で「リーン」と「スパイク的な理論空燃比またはリッチ空燃比(リッチスパイク)」を交互に繰り返されるように制御することを、リーン・リッチスパイク制御と称している。尚、この出願においては、リーン・リッチスパイク制御はリーン空燃比制御に含まれるものとする。

【0062】一方、燃料には硫黄(S)が含まれており、燃料中の硫黄が燃焼すると SO_2 や SO_3 などの硫黄酸化物(SO_x)が発生し、 NO_x 触媒17は排気ガス中のこれら SO_x も吸収する。 NO_x 触媒17の SO_x 吸収メカニズムは NO_x 吸収メカニズムと同じであると考えられる。即ち、 NO_x の吸収メカニズムを説明したときと同様に担体上に白金PtおよびバリウムBaを担持させた場合を例にとって説明すると、前述したように、排気空燃比がリーンのときには、酸素 O_2 が O_2^- 又は O^{2-} の形で NO_x 触媒17の白金Ptの表面に付着しており、流入排気ガス中の SO_x (例えば SO_2)は白金Ptの表面上で酸化されて SO_3 となる。

【0063】その後、生成された SO_3 は、白金Ptの表面で更に酸化されながらBa内に吸収されて酸化バリウム BaO と結合し、硫酸イオン SO_4^{2-} の形でBa内に拡散し硫酸塩 $BaSO_4$ を形成する。この $BaSO_4$ は結晶が粗大化し易く、比較的安定し易いため、一旦生成されると分解・放出されにくい。そして、 NO_x 触媒17中の $BaSO_4$ の生成量が増大すると NO_x 触媒17の吸収に関与できるBaOの量が減少して NO_x の吸収能力が低下してしまう。これが即ち SO_x 被毒である。したがって、 NO_x 触媒17の NO_x 吸収能力を高く維持するためには、適宜のタイミングで NO_x 触媒17に吸収された SO_x を放出させるための SO_x 被毒回復処理を実

行する必要がある。

【0064】NO_x触媒17からSO_xを放出させるためには、流入する排気ガスの空燃比を理論空燃比またはリッチ空燃比にする必要があり、また、NO_x触媒17の触媒温度が高いほど放出し易いことがわかっている。そこで、SO_x被毒回復処理は、NO_x触媒17の触媒温度をSO_xが放出され易い所定の高温（以下、これをSO_x放出温度という）にし、理論空燃比またはリッチ空燃比の排気ガスをNO_x触媒17に流すことにより実行する。

【0065】そして、この実施の形態では、SO_x被毒回復処理のために排気ガスの空燃比を理論空燃比またはリッチ空燃比にする場合も、燃料噴射弁11から噴射される燃料量をECU30により制御して燃焼室3に供給される混合気空燃比を理論空燃比またはリッチ空燃比に制御することにより行う。よって、ECU30と燃料噴射弁11は被毒回復手段の一部を構成する。

【0066】次に、この実施の形態における排気浄化装置のNO_x触媒17の熱劣化度合い検出方法について説明する。図5は、NO_x触媒17のSO_x被毒が所定レベルに達するたびに、NO_x触媒17に吸蔵されていたSO_xが完全に放出されるまでSO_x被毒回復処理を実行し、そのSO_x被毒回復直後のNO_x触媒17のNO_x浄化性能を測定した一実験結果をグラフにしたものである。NO_x触媒17のNO_x浄化性能は、SO_x被毒回復処理を実行する毎に低下している。

【0067】前述したように、NO_x触媒17のSO_x被毒劣化はSO_x被毒回復処理を実行することにより回復可能であるが、NO_x触媒17の熱劣化については被毒回復が不可能であることから、SO_x被毒回復処理直後の性能回復部分はSO_x被毒に起因した性能低下ということができ、性能回復不能部分は熱劣化に起因する性能低下といえることができる。

【0068】したがって、NO_x触媒17の新品時のNO_x吸蔵能力と、SO_x被毒回復処理直後のNO_x触媒17のNO_x吸蔵能力を検出することができれば、これらのNO_x吸蔵能力の差から熱劣化の度合いを検知することができる。

【0069】この実施の形態では、次のようにしてNO_x吸蔵能力を検出する。まず、NO_x触媒17にリーン空燃比の排気ガスを流し続けてNO_x触媒17のNO_x吸蔵能力を飽和させ、これ以上NO_xを吸蔵できない状態にする。次に、NO_x触媒17に流入する排気ガス、すなわち入ガスの空燃比をリーンからリッチに切り替え、リッチ空燃比の排気ガスをNO_x触媒17に流し続けて、NO_x触媒17に吸蔵されていたNO_xの全量を放出・還元させる。このとき、入ガスの空燃比をリーンからリッチに切り替えても、NO_x触媒17の出口の排気ガス、すなわち出ガスの空燃比は直ぐにはリッチに切り替わらず、しばらくの間は理論空燃比近傍になる。これは、N

O_x触媒17に吸蔵されていたNO_xの還元に入ガス中のHCやCOが還元剤として消費されるためである。そして、NO_x触媒17に吸蔵されていたNO_xの総てが放出・還元されて、入ガス中のHCやCOが還元剤として消費されなくなったときに、出ガスの空燃比がリッチに変わる。

【0070】したがって、このようにNO_x触媒17のNO_x吸蔵能力を飽和させた後にNO_xの放出・還元処理（以下、この処理のことを飽和NO_x放出処理という）を実行し、そのときの出ガスの空燃比を空燃比センサ27で検出し、飽和NO_x放出処理を開始してから出ガスの空燃比が理論空燃比を保持する時間、換言すれば出ガスの空燃比が理論空燃比からリッチに切り替わるまでの時間を計測すれば、その所要時間（以下、この所要時間をリッチ切り替わり時間という）はNO_x触媒17のNO_x吸蔵能力を表すバロメータになり、すなわちNO_x触媒17の浄化性能のバロメータになる。

【0071】図6は、飽和NO_x放出処理時における入ガスの空燃比と出ガスの空燃比の時間的変化の一例を示しており、新品のNO_x触媒17ではリッチ切り替わり時間が t_1 であるのに対して、熱劣化がある程度進行したNO_x触媒17のリッチ切り替わり時間は t_1 よりも短い t_2 になる。

【0072】また、この実施の形態では、NO_x触媒17に対してSO_x被毒回復処理を実行する時期の判定にも、リッチ切り替わり時間を用いて判定する。詳述すると、この実施の形態の排気浄化装置では、例えば一定の走行距離毎あるいは一定の燃料消費量毎などの適宜のタイミングでNO_x触媒17に対して飽和NO_x放出処理を実行し、そのときのリッチ切り替わり時間を計測する。そして、計測されたリッチ切り替わり時間が図6に示す所定時間 t_3 よりも短くなったときは、NO_x触媒17のNO_x浄化性能が所定レベルまで低下したものとみなすことができるので、このときをSO_x被毒回復処理を実行すべき時期であると判定する。

【0073】さらに、この実施の形態の排気浄化装置では、SO_x被毒回復処理の完了後に飽和NO_x放出処理を実行してリッチ切り替わり時間を計測し、計測されたリッチ切り替わり時間 t_2 と新品のNO_x触媒17のリッチ切り替わり時間 t_1 との差を算出し、その差が所定時間 t_4 よりも長くなったときには、NO_x触媒17の熱劣化が所定の度合いまで進んだと判断して、熱劣化を抑制すべく熱劣化抑制手段を作動する。なお、新品のNO_x触媒17のリッチ切り替わり時間 t_1 は予め実験的に求めてECU30のROM32に記憶しておき、また、熱劣化抑制手段を作動させるべきと判定するときの閾値 t_4 も予め設定してECU30のROMに記憶しておく。

【0074】次に、熱劣化の抑制方法について説明すると、たとえば、一般にエンジンでは減速運転になったときにはフューエルカットを実行しているが、熱劣化が所

定度合いまで進行したときには、エンジンが高温運転域にあるときに減速運転となったときにはフューエルカットを禁止することにより熱劣化を抑制することができる。これは、エンジンが高温運転域にあるとNOx触媒17も高温状態になっており、このときにフューエルカットを行うと酸素濃度が高い排気ガスがNOx触媒17に流入することになる。NOx触媒17における触媒物質(Pt)のシタリングは、触媒温度が同じ場合、酸素濃度が高いほどシタリングの進行速度が速いことが知られている。したがって、高温運転域の減速時にフューエルカットを行うと、触媒温度が高温のときに酸素濃度の高い排気ガスが流れることとなってシタリングを促進させてしまう。そこで、高温運転域にあるときに減速運転になったときにはフューエルカットを禁止すれば、NOx触媒17のシタリングを抑制し熱劣化を抑制することができる。この場合、高温運転域でのフューエルカットを禁止するフューエルカット禁止制御が熱劣化抑制手段を構成する。

【0075】また、別の熱劣化の抑制方法としては、熱劣化が所定度合いまで進行したときには、それ以前(すなわち、熱劣化が前記所定度合いまで進行していないとき)よりも、エンジンの高温運転域におけるリーン運転領域を減少せしめる方法がある。これも、前述と同じ理由であり、NOx触媒17の触媒温度が高いときには入ガスの酸素濃度を低くした方がNOx触媒17の熱劣化を抑制することができるからである。具体的な制御方法としては、熱劣化が所定度合いまで進行する以前に高温運転域で且つリーン運転領域であった領域の一部または全部を、熱劣化が所定度合いまで進行したとき以降はストイキ(理論空燃比)運転領域に変更する。この場合、高温運転域におけるリーン運転領域を減少するリーン運転領域減少制御が熱劣化抑制手段を構成する。

【0076】次に、図7を参照して、この実施の形態におけるNOx触媒17の熱劣化判定処理ルーチンを説明する。この制御ルーチンを構成する各ステップからなるフローチャートはECU30のROM32に記憶されており、この制御ルーチンは一定時間毎にCPU34によって実行される。

【0077】<ステップ101>まず、ECU100は、ステップ101において、NOx触媒17に対してSOx被毒回復処理を実行すべき時期か否かを判定する。前述したように、この実施の形態では、SOx被毒回復処理実行時期か否かの判定は、所定期間毎に飽和NOx放出処理を行い、そのときに計測したリッチ切り替わり時間が閾値t3よりも小さくなったときにSOx被毒回復処理を実行すべき時期であると判定する。ステップ101で否定判定した場合には、ECU30は、本ルーチンの実行を一旦終了する。

【0078】<ステップ102>ステップ101で肯定判定した場合には、ECU30は、ステップ102に進

み、SOx被毒回復処理を実行する。SOx被毒回復処理は、NOx触媒17がSOx放出温度に達していない場合には、所定の昇温処理を実行してNOx触媒17の触媒温度をSOx放出温度以上にし、且つ、NOx触媒17の入ガスの空燃比をストイキよりも若干リッチにすることにより行う。

【0079】<ステップ103>次に、ECU30は、ステップ103に進み、SOx被毒回復処理が完了したか否かを判定する。ここで、SOx被毒回復処理は、NOx触媒17に吸収されていたSOxをほぼ完全に放出するまで実行する。SOx被毒回復処理の完了の判定については後述する。ステップ103で否定判定した場合には、ECU30は、ステップ102に戻り、SOx被毒回復処理の実行を続行する。

【0080】<ステップ104, 105>ステップ103で肯定判定した場合には、ECU30は、ステップ104に進み、飽和NOx放出処理を実行し、さらに、ステップ105に進み、リッチ切り替わり時間tを計測する。

【0081】<ステップ106>次に、ECU30は、ステップ106に進み、予めECU30のROM32に記憶されている新品のNOx触媒17のリッチ切り替わり時間t1と、ステップ105で計測したリッチ切り替わり時間tとの差を算出する。すなわち、現時点のNOx触媒17の熱劣化度合いを算出する。

【0082】<ステップ107>次に、ECU30は、ステップ107に進み、ステップ106で算出したリッチ切り替わり時間の差(熱劣化度合い)が予め設定した閾値t4以上か否かを判定する。ステップ107で否定判定した場合には、ECU30は、本ルーチンの実行を一旦終了する。

【0083】<ステップ108>ステップ107で肯定判定した場合には、NOx触媒17の熱劣化度合いが所定レベルまで達したと判定して、ECU30は、ステップ108に進み熱劣化抑制手段を作動して、本ルーチンの実行を一旦終了する。熱劣化抑制手段の作動により、すなわち、前述した高温運転域におけるフューエルカット禁止制御の実行、あるいは、高温運転域におけるリーン運転領域減少制御の実行により、以後のNOx触媒17の熱劣化の進行が抑制される。

【0084】なお、この実施の形態においては、熱劣化判定処理ルーチンのうちECU30がステップ101を実行することにより本発明における被毒回復実行時期判定手段が実現され、また、ECU30がステップ102を実行することにより本発明における被毒回復手段が実現され、また、ECU30がステップ104およびステップ105を実行することにより本発明における吸蔵能力検出手段が実現され、また、ECU30がステップ106およびステップ107を実行することにより本発明における熱劣化判定手段が実現される。

【0085】次に、この実施の形態におけるSOx被毒回復処理について図8を参照して説明する。図8は、この実施の形態におけるSOx被毒回復処理時のNOx触媒17の入ガスの空燃比と、入ガスSOxセンサ23で検出された入ガスのSOx濃度と、出ガスSOxセンサ24で検出された出ガスのSOx濃度の経時変化を示した図である。なお、SOx被毒回復処理実行期間中、NOx触媒17の触媒温度はSOx放出温度以上になっているものとする。

【0086】まず、SOx被毒回復処理実行指令により入ガスの空燃比をリーン空燃比から理論空燃比に変更し、さらに入ガスの空燃比のリッチ度を漸次増大していく。そして、出ガスSOxセンサ24で検出された出ガスSOx濃度が入ガスSOxセンサ23で検出された入ガスSOx濃度に一致したとき、入ガスの空燃比を一致したときのリッチ空燃比で一定に保持する。出ガスSOx濃度が入ガスSOx濃度に一致した後は、実質的にNOx触媒17からSOxが放出されるため、出ガスSOx濃度の方が入ガスSOx濃度よりも大きくなり、所定濃度で出ガスSOx濃度がほぼ一定となる。さらにその後、NOx触媒17からのSOxの放出が続くと、NOx触媒17からのSOx放出量が減少するため、出ガスSOx濃度が低下していき、NOx触媒17に残留するSOxがなくなると、出ガスSOx濃度は入ガスSOx濃度よりも低くなっていく。したがって、出ガスSOx濃度が入ガスSOx濃度よりも所定値だけ低くなるまでSOx被毒回復処理を続行すれば、NOx触媒17をSOx被毒からほぼ完全に回復させたとみなすことができる。この実施の形態では、出ガスSOx濃度が図8において被毒回復完了レベル以下になるまでSOx被毒回復処理を続行することにした。

【0087】〔第2の実施の形態〕この実施の形態では、排気浄化装置のNOx触媒17の熱劣化度合いを、NOx触媒のNOx浄化率の変化に基づいて検出する場合について説明する。図13はこの実施の形態における排気浄化装置の概略図であり、機関本体40には4個の気筒41が設けられ、各気筒41に接続される吸気ポートには燃料噴射弁42が取り付けられている。吸気マニホールド43は、吸気ダクト44を介してエアクリーナ45に連結されている。また吸気ダクト44内には、スロットル弁46が設けられている。

【0088】一方、排気マニホールド47及び排気管48を介して、吸蔵還元型NOx触媒50を内蔵したケーシング49に接続され、ケーシング49は排気管51を介して図示しないマフラーに接続されている。その他のECU30、NOx触媒17等の構成については、第1の実施の形態における排気浄化装置と同様であるので、同一の符号を付して説明を省略する。

【0089】ケーシング49の下流には、NOx触媒17から流出する出ガスのNOx濃度に比例した出力電圧

を発生する出ガスNOxセンサ50が設けられ、この出力電圧はECU30の入力ポート35に入力される。図14は、NOx触媒17によるNOx浄化率の一例を示す図である。ここで入NOxとは、NOx触媒17に流入する排気ガス中の単位時間あたりのNOx濃度を示し、出NOxとは、NOx触媒17から流出する排気ガス中の単位時間あたりのNOx濃度を示す。ここではNOx触媒17から排出される排気ガス中の単位時間あたりのNOx濃度が閾値Xに到達すると、排気ガスをストイキまたはリッチにしてNOx触媒17に吸蔵されているNOxを放出、還元させてNOx触媒17のNOx吸蔵能力を回復させる。しかし排気ガスがリーンの状態での運転が継続して排気ガス中のNOxがNOx触媒17に吸蔵されると、再び飽和状態に達して、出NOxの濃度が閾値Xに達する。そこで再びリッチスパイクを実行することでNOxを放出、還元する。

【0090】しかしこれを繰り返すと、第1の実施の形態において詳説したように、NOx触媒17のSOx被毒が所定レベルに達するので、SOx被毒回復処理を実行することになる。そしてNOx触媒17のSOx被毒はSOx被毒回復処理を実行することで回復可能であるが、NOx触媒17の熱劣化は回復することができないので、SOx被毒回復処理直後の性能回復不能部分は、熱劣化に起因する性能低下であることができる。

【0091】したがってNOx触媒17の新品時のNOx浄化率と、そのSOx被毒回復処理直後のNOx浄化率とを測定し、これを比較すればそのNOx浄化性能の差から熱劣化の度合いを知ることができる。ここでNOx浄化率とは、NOx触媒に流入する排気ガス中のNOx量（入NOx量）と、NOx触媒の下流に設置したNOx検出手段による排気ガス中のNOx量（出NOx量）に基づいて求められる。このとき前記入NOxの量は、NOx触媒17の上流の排気通路にNOxセンサを取り付けることで、その出力値から単位時間あたりのNOx濃度と排気ガス量の積算値から算出することができる。また入NOxの量は次のような方法によっても求められる。

【0092】すなわち、リーン混合気が燃焼しているときは機関負荷が高くなるほど単位時間あたり機関から排出されるNOx量が増大し、また機関回転数が高くなるほど単位時間あたりの機関から排出されるNOx量が増大する。したがって単位時間あたりのNOx量は機関負荷と機関回転数の関数となる。この場合、機関負荷はサージタンク内の絶対圧によって代表することができるので、単位時間あたりの出NOxの量NOXAは、サージタンク内の絶対圧PMと機関回転数Nの関数となる。よってこの実施の形態では、単位時間あたりのNOx量を絶対圧PM及び機関回転数Nの関数として予め実験により求め、これを図16に示すようなマップの形でECU30のRAM内に記憶しておく。

【0093】一方、NOx触媒17の下流の排気通路に

NO_xセンサを取り付けることで、その出力値から単位時間あたりのNO_x濃度が検出されるので、出NO_xの量は、このNO_x濃度と排気ガス量の積算値に基づいて算出することができる。このようにして、NO_x触媒17のNO_x浄化率を測定し、これを初期の新品の場合の浄化率または必要浄化率と比較することで、SO_x被毒再生の時期を判断することができる。

【0094】また、NO_x触媒17の新品時のNO_x浄化率と、SO_x被毒回復処理直後のNO_x触媒17のNO_x浄化率を検出し、これらを比較することができれば、それらの浄化率の差からNO_x触媒17の熱劣化の度合いを検知することができる。なお、新品のNO_x触媒17のNO_x浄化率及び必要浄化率は、予め実験的に求めてECU30のROM32に記憶しておき、また、熱劣化抑制手段を作動させるべきと判定するときの必要浄化率も予め設定してECU30のROMに記憶しておく。

【0095】この実施の形態では、以下のようにしてNO_x浄化性能を検出する。まず、NO_x触媒17にリーン空燃比の排気ガスを流し続けてNO_x触媒17のNO_x吸蔵能力を飽和させ、これ以上NO_xを吸蔵できない状態にする。このとき、NO_x触媒の浄化性能を温度ウインドウを考慮して測定する。

【0096】次に、NO_x触媒17に流入する排気ガス、すなわち入ガスの空燃比をリーンからリッチに切り替え、リッチ空燃比の排気ガスをNO_x触媒17に流し続けて、NO_x触媒17に吸蔵されていたNO_xの全量を放出・還元させる。このとき、入ガスの空燃比をリーンからリッチに切り替えても、NO_x触媒17の出口の排気ガス、すなわち出ガスの空燃比は直ぐにはリッチに切り替わらず、しばらくの間は理論空燃比近傍になる。これは、NO_x触媒17に吸蔵されていたNO_xの還元に入ガス中のHCやCOが還元剤として消費されるためである。そして、NO_x触媒17に吸蔵されていたNO_xの総てが放出、還元されて、入ガス中のHCやCOが還元剤として消費されなくなったときに、出ガスの空燃比がリッチに変わる。

【0097】また、この実施の形態では、NO_x触媒17に対してSO_x被毒回復処理を実行する時期の判定には、NO_x浄化率が所定値以下になったか否かにより判断する。詳述すると、この実施の形態の排気浄化装置では、例えば一定の走行距離毎あるいは一定の燃料消費量毎などの適宜のタイミングでNO_x触媒17に対して飽和NO_x放出処理を実行し、そのときのNO_x浄化率を測定する。この測定は出側NO_xセンサ50により、各負荷、温度条件でのNO_x触媒の浄化性能を把握しする。

【0098】そして、測定されたNO_x浄化率が図14に示す閾値xよりも低下したときは、NO_x触媒17のNO_x浄化性能が所定レベルまで低下したものとみなす。またこのときをSO_x被毒回復処理を実行すべき時期であると判定する。

【0099】SO_x被毒回復処理が完了したらNO_x浄化率を測定し、NO_x触媒の性能が回復したか否かを判断する。これは図15に示すように、NO_x浄化率が、所定温度（例えば、300℃～420℃程度）の範囲において、必要浄化率を上回ったか否かにより判断する。図15では、①がNO_x触媒が新品時であるときのNO_x浄化率を示し、②はSO_x被毒時のNO_x浄化率を示す。②の状態ではSO_x被毒回復が必要な状態であり、③はSO_x被毒回復後の浄化率を示している。

【0100】必要浄化率が確保されない場合は、次に、NO_x触媒の熱劣化の度合いに応じたリッチスパイクを実行する。これは内燃機関においてリーン混合気の燃焼が行われている場合、即ち中低負荷運転を行っているときには、比較的短い周期でスパイク的（短時間）にストイキまたはリッチ混合気の燃焼が行われるように混合気の空燃比を制御し、短周期的にNO_xの放出・還元を行っているが、性能低下の回復が不十分であれば、リッチスパイクを増加させる。これはリッチスパイクの量の増大、またはリッチスパイクの回数の増大、すなわちリッチスパイクの周期の短縮化の両方があり、いずれか一方、または両方を、熱劣化の度合いに比例するようにして実行する。

【0101】次に、この実施の形態の排気浄化装置では、前記リッチスパイク制御を実施した後、NO_x浄化率を測定し、その浄化率が所定レベル以下のときは、NO_x触媒17の熱劣化が性能回復が不可能な程度まで進んだと判断して、熱劣化を抑制すべく熱劣化抑制手段を作動する。すなわちこのような制御を実施しても十分なNO_x浄化率が確保できない場合である。

【0102】先ず、性能不足の温度領域でのリーン運転を禁止する。これは熱劣化が所定度合いまで進行していないときよりも、リーン運転領域を減少させて、NO_x触媒17の入ガス酸素濃度を低くすることでNO_x触媒17の熱劣化を抑制するものである。具体的には図15に示すように、NO_x触媒の性能が必要浄化率以下になる温度領域（回復しても戻らない領域）において、リーン運転を禁止してこの領域をストイキ運転領域に変更するものである。

【0103】次に、これとは別の熱劣化の抑制方法として、または前記と併せて実行する熱劣化の抑制方法として、第1の実施の形態において説明したように、エンジンが高温運転域にあるときに減速運転となったときでも、フューエルカットを禁止することにより熱劣化を抑制する。また熱劣化の抑制方法として、熱劣化が所定度合いまで進行していないときよりも、エンジンの高温運転域におけるリーン運転領域を減少させる方法を採用する。これは上述した性能不足の温度領域でのリーン運転の禁止の範囲と重複するが、所定温度以上の高温運転領域では全てリーン運転を禁止するものである。

【0104】以下、図17を参照して、この実施の形態

におけるNOx触媒17の熱劣化判定処理ルーチンを説明する。この制御ルーチンを構成する各ステップからなるフローチャートはECU30のROM32に記憶されており、この制御ルーチンは一定時間毎にCPU34によって実行される。

【0105】<ステップ201>まず、ECU100は、ステップ201において、NOx触媒17に対してSOx被毒回復処理を実行すべき時期か否かを判定する。SOx被毒回復処理実行時期か否かの判定は、所定期間毎に飽和NOx放出処理を行い、放出処理の完了後にNOx浄化率を測定する。これは出側のNOxセンサ50の出力値に基づいて算出する。この値が必要浄化率よりも低くなったときをSOx被毒回復処理を実行すべき時期であると判定する。ステップ201で否定判定した場合には、ECU30は、本ルーチンの実行を一旦終了する。

【0106】<ステップ202>ステップ201で肯定判定した場合には、ECU30は、ステップ202に進み、SOx被毒回復処理を実行する。SOx被毒回復処理は、NOx触媒17がSOx放出温度に達していない場合には、所定の昇温処理を実行してNOx触媒17の触媒温度をSOx放出温度以上にし、且つ、NOx触媒17の入ガスの空燃比をストイキよりも若干リッチにすることにより行う。

【0107】<ステップ203>次に、ECU30は、ステップ203に進み、SOx被毒回復処理が完了したか否かを判定する。ここで、SOx被毒回復処理は、NOx触媒17に吸収されていたSOxをほぼ完全に放出するまで実行する。ステップ203で否定判定した場合には、ECU30は、ステップ202に戻り、SOx被毒回復処理の実行を続行する。

【0108】<ステップ204>ステップ203で肯定判定した場合には、ECU30は、ステップ204に進み、飽和NOx放出処理を実行し、さらに、ステップ205に進み、NOx浄化率を測定する。

【0109】<ステップ205>次に、ECU30は、ステップ205に進み、NOx触媒17のNOx浄化率を測定する。

【0110】<ステップ206>ステップ206に進み、ECU30は、ステップ206で測定したNOx浄化率が予め設定した必要浄化率以上となり、NOx触媒機能が回復したか否かを判定する。ステップ206で肯定判定した場合には、ECU30は、本ルーチンの実行を一旦終了する。

【0111】<ステップ207>ステップ206で否定判定した場合には、リッチスバイク制御を実行して、NOx触媒17の性能を試みる。

【0112】<ステップ208>ステップ207で実行されたリッチスバイク制御によって、NOx触媒のNOx浄化率が回復したか否かを判断する。これは所定の温度

範囲におけるNOx浄化率が必要浄化率よりも低いかなによって判断される。浄化率が必要浄化率以上であればECU30は、本ルーチンの実行を一旦終了する。

【0113】<ステップ209>ステップ208においてNOx浄化率が必要浄化率以下であれば、性能が不足する温度領域におけるリーン運転を禁止する。NOx浄化率が必要浄化率以下でるときは、性能回復は不可能とされ、熱劣化が大きいものと判断される。

【0114】<ステップ210>さらに他の熱劣化抑制制御を実施する。これは高温運転領域でのリーン運転領域の減少及び高温運転域でのフェールカット禁止の制御である。これにより以後のNOx触媒17の熱劣化の進行が抑制される。

【0115】なお、この実施の形態においては、熱劣化判定処理ルーチンのうちECU30がステップ201を実行することにより第2の発明における被毒回復実行時期判定手段が実現され、また、ECU30がステップ202を実行することにより被毒回復手段が実現され、また、ECU30がステップ204およびステップ205を実行することによりNOx浄化率測定手段が実現される。

【0116】また、この実施の形態においてリッチスバイク制御によってNOx浄化率が確保されない場合、NOx触媒17の熱劣化が大きいと判断して、触媒の交換を促すようにすることができる。

【0117】〔他の実施の形態〕SOx被毒回復処理実行完了の判定は、SOx被毒回復処理実行時間が予め設定した所定時間を超えたか否かで判定することができる。この場合には、NOx触媒17に吸蔵されたSOxをほぼ完全に放出するために必要な被毒回復処理時間を予め実験的に求め、これをECU30のROM32に記憶させておく。

【0118】SOx被毒回復処理実行時期か否かの判定は、NOx触媒17を通過する硫黄量が所定量（以下、許容硫黄量という）を越えたときがSOx被毒回復処理実行時期であると判定してもよい。

【0119】その場合、入ガスSOxセンサ23で検出された入ガスのSOx濃度から燃料中の硫黄濃度を推定し、この燃料中の推定硫黄濃度に基づいて前記許容硫黄量に対応する燃料消費量あるいは走行距離を算出して、その燃料消費量あるいは走行距離に達したときをSOx被毒回復処理実行時期であると判定することができる。さらに、この場合には、燃料中の推定硫黄濃度を運転席前のパネル等に表示して、SOx被毒回復処理の頻度がおおよそ判別できるようにしてもよい。

【0120】あるいは、入ガスSOxセンサ23で検出された入ガスのSOx濃度とエンジンの吸入空気量に基づいて、NOx触媒17に流入するSOx量を算出し、その積算値が所定量を越えたときを、SOx被毒回復処理実行時期であると判定することができる。

【0121】このようにNOx触媒17を通過する硫黄量が許容硫黄量を越えたときをSOx被毒回復処理実行時期であると判定し、且つ、前述の如くSOx被毒回復処理実行完了の判定をSOx被毒回復処理実行時間で行う場合には、出ガスSOxセンサ24を省略することができる。

【0122】また、SOx被毒回復処理実行時期か否かの判定は、NOx触媒17に吸蔵されたSOx量を推定し、この推定吸蔵SOx量が所定量を越えたときがSOx被毒回復処理実行時期であると判定してもよい。なお、吸蔵SOx量の推定は、図9に示すように、入ガスSOxセンサ23で検出された入ガスのSOx濃度と出ガスSOxセンサ24で検出された出ガスのSOx濃度の濃度差分がNOx触媒17に吸蔵されるものとして、このSOx濃度差（入ガスSOx濃度－出ガスSOx濃度）とエンジンの吸入空気量に基づいて算出することができる。そして、このようにして算出推定した吸蔵SOx量をSOx堆積カウンタで積算して、SOx堆積カウンタのカウント値が所定値を越えたときをSOx被毒回復処理実行時期であると判定することができる。

【0123】また、このようにSOx堆積カウンタを備えた場合には、SOx被毒回復処理の完了の判定を次のようにすることもできる。SOx被毒回復処理実行期間中であって出ガスSOx濃度が入ガスSOx濃度より大きい期間においては、出ガスSOx濃度と入ガスSOx濃度の濃度差分がNOx触媒17から放出されるSOxであると推定することができるので、このSOx濃度差（出ガスSOx濃度－入ガスSOx濃度）とエンジンの吸入空気量に基づいてNOx触媒17から放出されたSOx量を算出し、算出推定したSOx放出量を前記SOx堆積カウンタで減算し、図10に示すようにSOx堆積カウンタのカウント値が所定値（被毒回復完了レベル）まで低下したときに、SOx被毒回復処理が完了したものとしてSOx被毒回復処理の実行を終了することができる。

【0124】さらに、SOx被毒回復処理実行時期か否かの判定は、出ガスのSOx濃度が入ガスのSOx濃度に所定レベルまで接近したときをSOx被毒回復処理実行時期であると判定してもよい。図11に示すように、NOx触媒17の出ガスのSOx濃度は、SOx被毒が進行するにしたがって入ガスのSOx濃度に接近してくる。したがって、出ガスのSOx濃度の入ガスのSOx濃度への接近の程度は、SOx被毒の度合いに対応していると言うことができる。そこで、予め出ガスのSOx濃度がどの程度まで入ガスのSOx濃度に接近したときにSOx被毒回復処理を実行するかを設定しておき、出ガスSOxセンサ24で検出された出ガスのSOx濃度が前記設定したSOx濃度を越えたときをSOx被毒回復処理実行時期であると判定することができる。

【0125】前述の各実施の形態では、NOx触媒17の上流に入ガスSOxセンサ23を設け、この入ガスS

Oxセンサ23によりNOx触媒17に流入する排気ガスのSOx濃度を検出しているが、NOx触媒17に流入する排気ガスのSOx濃度は燃料中の硫黄濃度と燃料量と排気ガス量に依存するので、燃料中の硫黄濃度が既知である場合には、エンジン運転状態（燃料噴射量、空燃比、吸入空気量、エンジン回転数など）から推定することが可能である。したがって、その場合には、入ガスSOxセンサ23を設ける代わりに、エンジン運転状態からECU30により触媒入ガスのSOx濃度を算出し、推定するようにしてもよい。

【0126】前述した実施の形態では本発明をガソリンエンジンに適用した例で説明したが、本発明をディーゼルエンジンに適用することができることは勿論である。ディーゼルエンジンの場合は、燃焼室での燃焼がストイキよりもはるかにリーン域で行われるので、通常の機関運転状態ではNOx触媒17に流入する排気ガスの空燃比は非常にリーンであり、NOx及びSOxの吸収は行われるものの、NOx及びSOxの放出が行われることは殆どない。

【0127】また、ガソリンエンジンの場合には、前述したように燃焼室3に供給する混合気をストイキあるいはリッチにすることにより排気空燃比をストイキあるいはリッチにし、排気ガス中の酸素濃度を低下させて、NOx触媒17に吸収されているNOxやSOxを放出させることができるが、ディーゼルエンジンの場合には、燃焼室に供給する混合気をストイキあるいはリッチにすると燃焼の際に煤が発生するなどの問題があり採用することはできない。

【0128】したがって、本発明をディーゼルエンジンに適用する場合、排気空燃比をストイキあるいはリッチにするためには、機関出力を得るために燃料を燃焼するのは別に、還元剤（例えば燃料である軽油）を排気ガス中に供給する必要がある。排気ガスへの還元剤の供給は、吸気行程や膨張行程や排気行程において気筒内に燃料を副噴射することによっても可能であるし、あるいは、NOx触媒17の上流の排気通路内に還元剤を供給することによっても可能である。

【0129】尚、ディーゼルエンジンであっても排気再循環装置（所謂、EGR装置）を備えている場合には、排気再循環ガスを多量に燃焼室に導入することによって、排気ガスの空燃比を理論空燃比またはリッチ空燃比にすることが可能である。

【0130】

【発明の効果】本発明にかかる内燃機関の排気浄化装置によれば、吸蔵還元型NOx触媒の熱劣化度合いを判定する熱劣化判定手段を備えることにより、吸蔵還元型NOx触媒の熱劣化度合いを判定することができる。したがってNOx浄化性能が低下してこれが回復できないものであることを知ることができ、触媒の交換等によって排気ガス中のNOxが浄化されなくなる状況を回避でき

る。

【0131】また本発明にかかる内燃機関の排気浄化装置は、前記吸蔵還元型NOx触媒の熱劣化を抑制する熱劣化抑制手段を備え、この熱劣化抑制手段は、前記熱劣化判定手段により判定された熱劣化度合いが所定レベル以下のときには作動せず、前記所定レベルを超えたときに作動するようにした場合には、吸蔵還元型NOx触媒の熱劣化度合いが前記所定レベルに達した以後の熱劣化の進行を抑制することができる。

【図面の簡単な説明】

【図1】 本発明に係る内燃機関の排気浄化装置の第1の実施の形態の概略構成図である。

【図2】 基本燃料噴射時間のマップの一例を示す図である。

【図3】 機関から排出される排気ガス中の未燃HC、COおよび酸素の濃度を概略的に示す線図である。

【図4】 吸蔵還元型NOx触媒のNOx吸放出作用を説明するための図である。

【図5】 吸蔵還元型NOx触媒の劣化の進み具合を示す図である。

【図6】 前記第1の実施の形態における飽和NOx放出処理時の出ガスの空燃比の経時変化を示す図である。

【図7】 前記第1の実施の形態における熱劣化判定処理ルーチンを示すフローチャートである。

【図8】 前記第1の実施の形態におけるSOx被毒回復処理時の入ガスの空燃比と出ガスのSOx濃度の経時変化を示す図である。

【図9】 本発明にかかる内燃機関の排気浄化装置におけるSOx被毒回復処理の実行時期を判定する方法を説明する図である。

【図10】 本発明にかかる内燃機関の排気浄化装置におけるSOx被毒回復処理の完了を判定する方法を説明する図である。

*

*【図11】 本発明にかかる内燃機関の排気浄化装置におけるSOx被毒回復処理の実行時期を判定する方法を説明する図である。

【図12】 触媒物質のシンタリングと吸蔵還元型NOx触媒のNOx浄化性能との関係を示す図である。

【図13】 第2の実施の形態にかかる内燃機関の排気浄化装置の概略図である。

【図14】 本発明にかかる内燃機関の排気浄化装置におけるNOx浄化率の変化を示す図である。

10. 【図15】 本発明にかかる内燃機関の排気浄化装置における吸蔵還元型NOx触媒のSOx被毒回復処理を説明するための図である。

【図16】 入NOx量の決定に使用する数値テーブルを示す図である。

【図17】 前記第1の実施の形態における熱劣化判定処理ルーチンを示すフローチャートである。

【符号の説明】

1、40 エンジン本体（内燃機関）

3 燃焼室

20 4 点火栓

11、42 燃料噴射弁（被毒回復手段）

16、48 排気管（排気通路）

17 吸蔵還元型NOx触媒

18、49 ケーシング

19、51 排気管（排気通路）

21、45 エアフロメータ

23 入ガスSOxセンサ（入ガスSOx濃度検出手段）

24 出ガスSOxセンサ（出ガスSOx濃度検出手段）

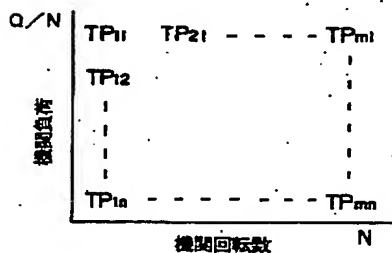
25 温度センサ

30 27 空燃比センサ

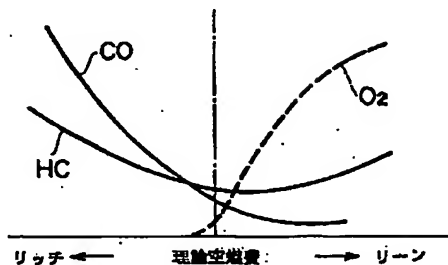
30 ECU

50 出ガスNOxセンサ（出ガスNOx濃度検出手段）

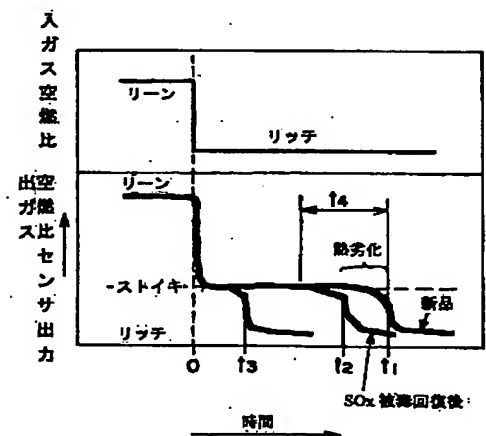
【図2】



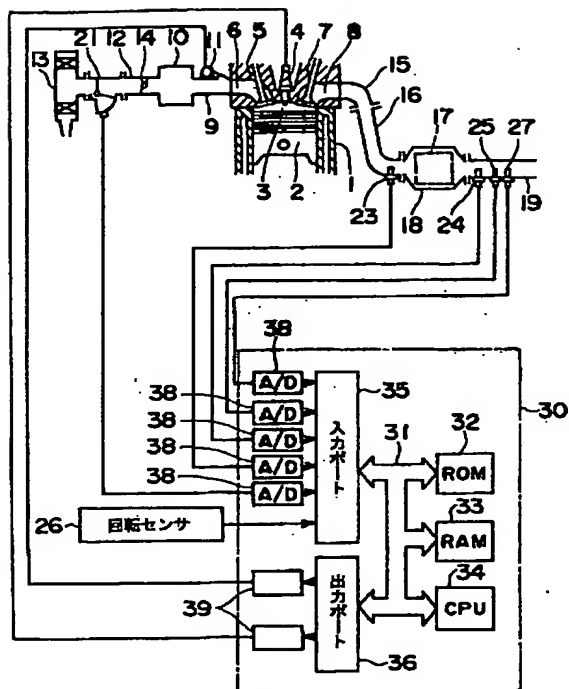
【図3】



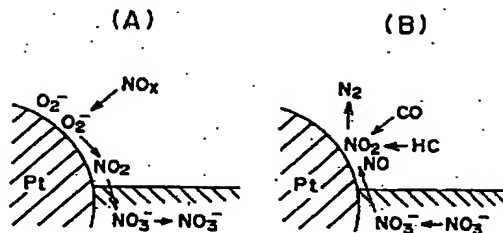
【図6】



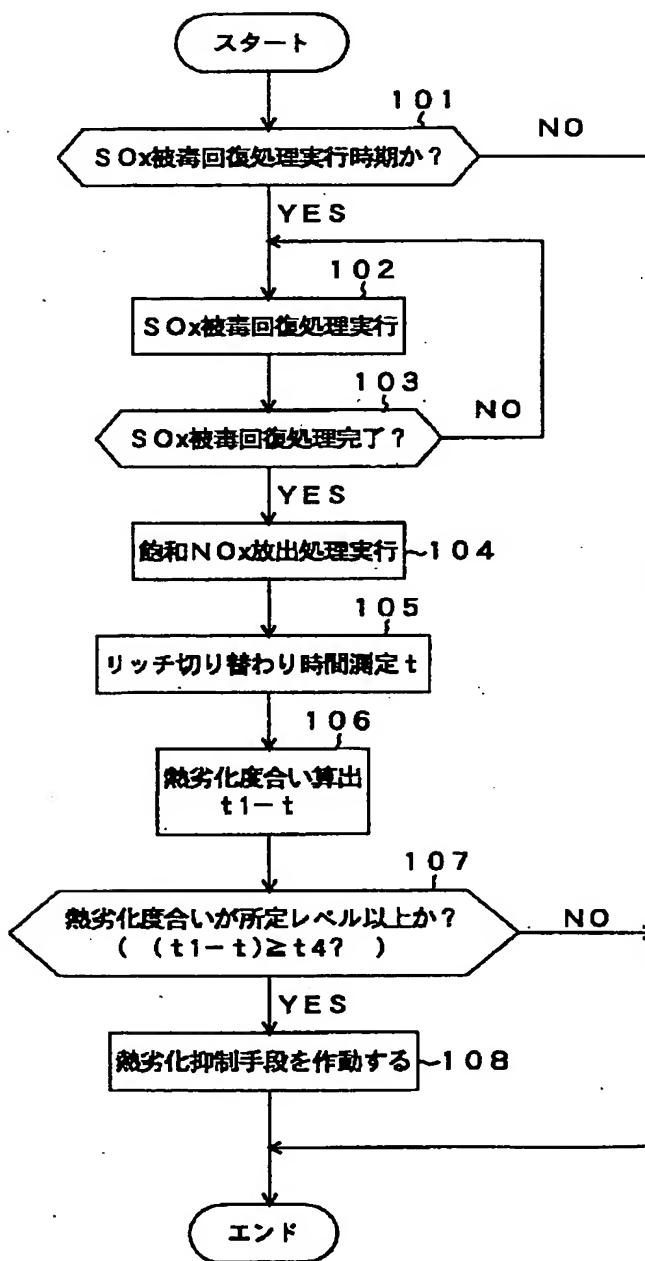
【図1】



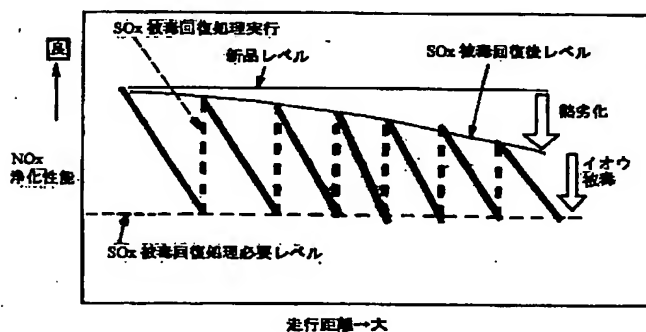
【図4】



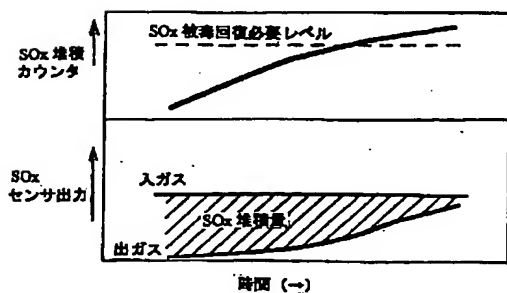
【図7】



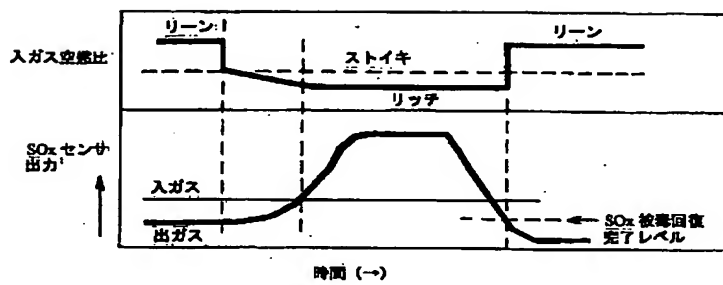
【図5】



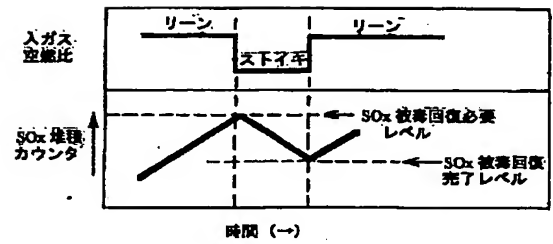
【図9】



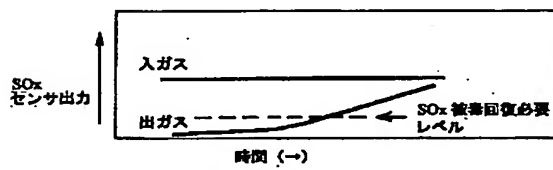
【図8】



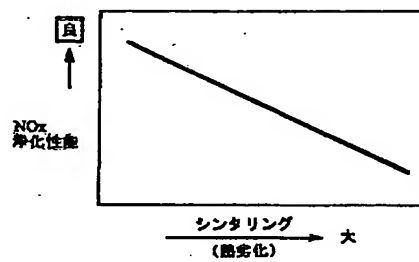
【図10】



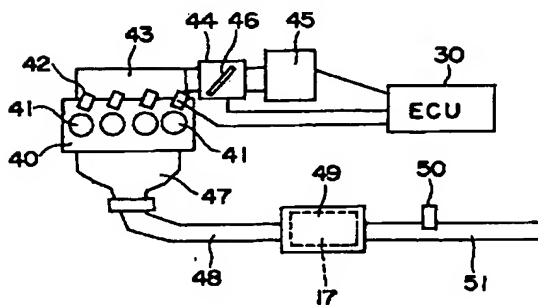
【図11】



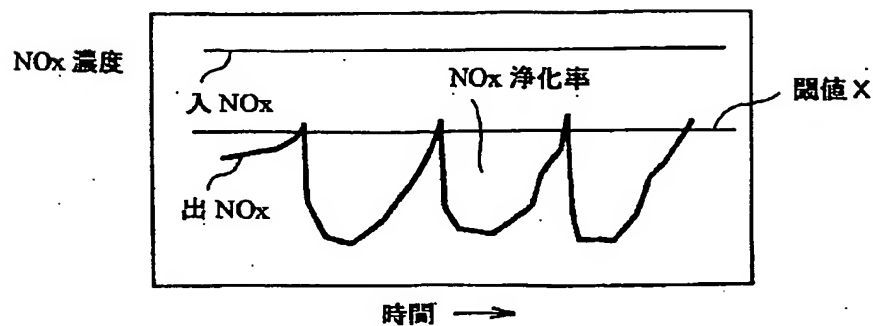
【図12】



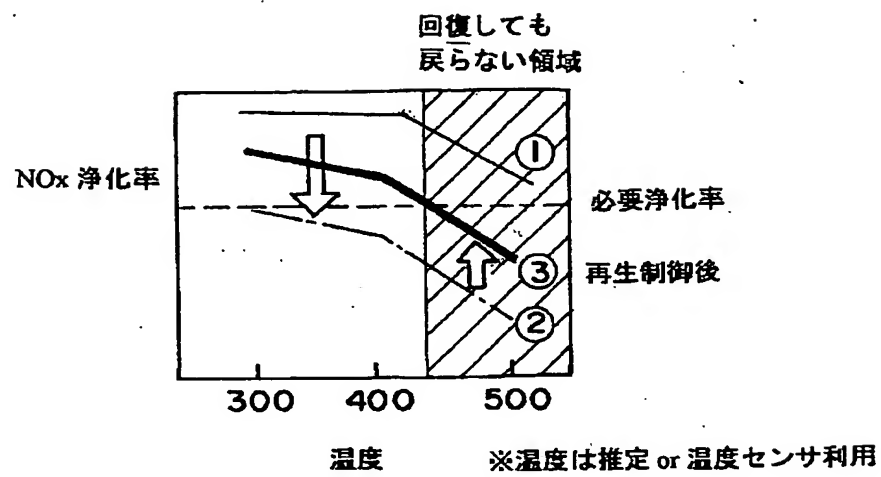
【図13】



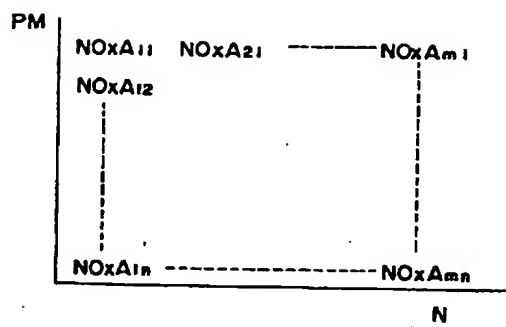
【図14】



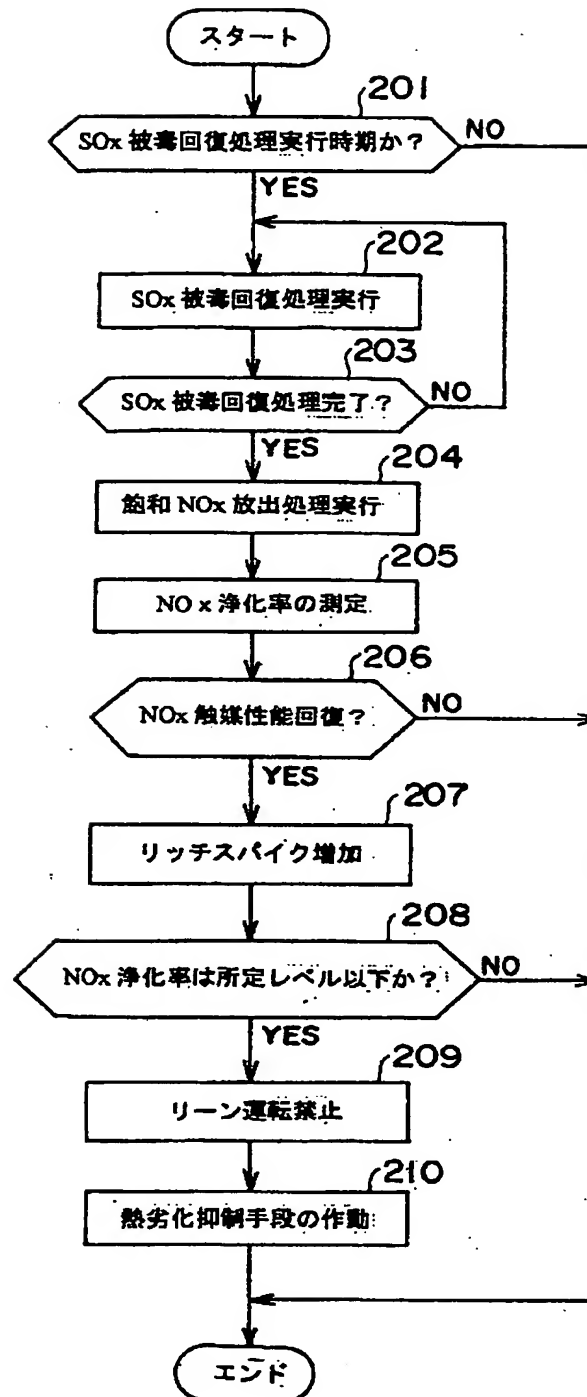
【図15】



【図16】



【図17】



フロントページの続き

(51)Int.Cl.

F 0 2 D 41/04
41/12

識別記号

3 0 5
3 3 0

F I

F 0 2 D 41/12
45/00

テーマコード (参考)

3 3 0 K
3 1 4 Z

45/00

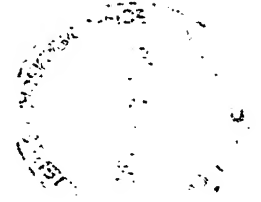
3 1 4

B O I D 53/36

1 0 1 B

1 0 1 A

F ターム(参考) 3G084 AA04 BA11 BA13 BA16 DA10
DA19 DA22 EA03 EA08 EA11
EB08 EB12 EB16 FA07 FA26
FA27 FA28 FA33
3G091 AA12 AA17 AA23 AB06 BA11
BA33 CB02 DA07 DA10 DB10
DC01 DC03 EA01 EA05 EA07
EA33 FA05 FB10 FC01 GB03Z
GB06Z HA36 HA37 HA42
3G301 HA01 HA15 JA15 JA25 JA33
KA16 LB02 LC01 MA01 MA11
MA24 NA08 NC04 ND02 NE06
PA01Z PA11Z PD08Z PD09Z
PE01Z
4D048 AA06 AB07 BA03X BA14X
BA15X BA18X BA30X BA41X
BC01 BD02 CD06 DA01 DA02
DA03 DA05 DA08 DA20 EA04



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.